KINETICS AND EQUILIBRIA OF CADMIUM IN SELECTED KENYAN SOILS

A Thesis

Submitted to the College of Graduate Studies and Research

in Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

in the

Department of Soil Science

University of Saskatchewan

Saskatoon, Saskatchewan, Canada

by

John Onam Onyatta

Fall, 1997

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Head of the Department of Soil Science
University of Saskatchewan
51 Campus Drive
Saskatoon, Saskatchewan
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ABSTRACT

Cadmium (Cd) is ubiquitous in agricultural soils and is of concern because of its potential toxicity to the ecosystem. The objectives of this study were to investigate (1) the Cd status and speciation and the fate of applied Cd in selected tropical soils in Kenya and (2) the effect of soil properties, low-molecular-weight organic acids (LMWOAs), and the application of monoammonium phosphate (MAP) and potassium chloride (KCl) fertilizers on the kinetics of Cd in the soils.

The total Cd and the Cd availability index (CAI) which was taken as ammonium acetate-acetic acid-ethylene diamine tetraacetic acid (AAAc-EDTA) extractable Cd generally decreased with depth and varied with the soil type. Exchangeable and carbonate-bound Cd were not detected in the natural tropical soils studied. Metal-organic complex bound-Cd was the most predominant in the surface soils, whereas in the subsurface soils, Cd was present mainly in the residual form. Metal-organic complex-bound Cd significantly contributed to the CAI of the soils studied.

With increasing residence time, the Cd added to the soils in the form of the Idaho MAP-fertilizer was transformed to a series of particulate-bound Cd species. The residual Cd species steadily increased, whereas the rest of the particulate-bound Cd species decreased. The M NH_4Cl extractable Cd also decreased with the residence time and the extent of the decrease depended upon the soil type.

The LMWOAs influenced the Cd released from the natural soils and the soils treated with the Idaho MAP-fertilizer to solution through the formation of Cd-LMWOA

complexes. The LMWOAs commonly present in the soil rhizosphere were effective in mobilizing the soil Cd, especially in the phosphate treated soils.

The KCl fertilizer promoted the release of Cd from the soils particularly after treatment with the Idaho MAP-fertilizer. The release of Cd to solution by KCl was attributed to the combined effects of Cd-chloride complexation and ionic strength.

The application of Idaho MAP-fertilizer greatly enhanced Cd released from the soils. Ammonium taranakite was identified as a reaction product in the MAP treated acidic tropical soils using X-ray diffraction analysis. In the fertilizer granule-soil interface, the formation of NH_4-taranakite may be perturbed by Cd, if the applied MAP fertilizer contains sufficiently high Cd as an impurity.

The findings obtained in the present study are fundamental for establishing a Cd database and are of significance in interpreting the importance of speciation, dynamics and fate of Cd in its bioavailability in tropical soils. The impact of farming practices such as crops and cropping systems and application of fertilizers on Cd contamination of the food chain deserves attention.

ACKNOWLEDGMENTS

I wish to express my sincere thanks to my supervisor Prof. P. M. Huang for his guidance and patience . I am grateful for his encouragement throughout my study.

I wish to thank members of my Advisory Committee, Professors E. de Jong, J. W. Quail, H. Tiessen and K. C. J. Van Rees for their constructive criticisms and suggestions. I also wish to thank Prof. L. M. Shuman, the external examiner for his critiques and suggestions.

I wish to acknowledge the assistance and the friendship of the members of Prof. P. M. Huang's Soil Physical Chemistry Laboratory.

My appreciation is also extended to my employer, Egerton University and the Kenya Government for giving me leave of absence in my pursuit for knowledge.

The financial support from the Canadian International Development Agency (CIDA) is gratefully acknowledged.

Finally, I would like to thank my family, my wife Rosemary Achieng Onam and children Ken and Larissa for putting up with the difficulties and hardships during my absence from home, especially when my wife lost all her parents and was soon followed by the loss of my mother. Without their love and support none of this would have been possible.

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1. INTRODUCTION

Cadmium is one of the most toxic and mobile metallic elements in soils. The presence of Cd in agricultural ecosystems is of concern because of high toxicity and affinity of Cd for biological tissue. Cadmium is considered a non-essential element for plants and animals but is a contaminant in the human diet and accumulates in the body over time leading to health problems such as kidney dysfunction and osteomalacia (Fergusson, 1990). Cadmium is present in the soil parent material. Furthermore, the soil environment is a storage site for Cd and other trace metals introduced through atmospheric deposition and application of sewage sludges, or phosphate fertilizers, and thus, forms an important pathway for Cd contamination to the terrestrial food chain

The interactions of Cd in the environment are complicated by the presence of inorganic and organic substances capable of binding with Cd to form soluble complexes and chelates (Sakurai and Huang, 1995). The ability of a soil to adsorb and retain heavy metals merits attention since the soil retention capacity is a complex function of the soil system parameters and the chemistry of the metals under the existing conditions (Elliot and Denney, 1982). The potential toxicity of Cd to human has encouraged research into the presence of this metal in soils, with particular emphasis on soils treated with sewage sludge or phosphate fertilizers (Rothbaum et al., 1986; McGrath and Cegarra, 1992; De Boo, 1990) and those exposed to some Cd polluting source (Hickey and Kittrick, 1984; Xian, 1988; Jensen and Bro-Rasmussen, 1992). Cadmium introduced into agricultural soils through anthropogenic sources can undergo transformations with time. The fate of Cd from anthropogenic sources depends essentially on its retention and mobility in the soil. Changes in the forms of Cd with time could affect its uptake by plants and hence its

potential toxicity to human health. The extent of Cd build-up in soils varies with the type of soil, Cd content in the fertilizers and the management practices involved (Mortvedt and Osborn 1982; Tiller et al., 1984; Alloway 1995; Mann and Ritchie 1993). The effect of time on retention of Cd by soils may have important implications for Cd uptake by plants and hence its contamination of the food chain. The plant uptake of Cd can vary greatly depending on the plant species and cultivar (Haghiri, 1973; Bingham et al. 1984), the soil type (Williams and David, 1973; Miller et al., 1976), the farming practices (Andersson and Nilsson, 1974; Jackson and Alloway, 1991; He and Singh, 1994a) and the environmental conditions (Jackson and Alloway, 1992; Alloway, 1995).

The forms in which Cd may exist in different soil horizons and their distribution depend on the physical, chemical and mineralogical properties of the soil (Ramos et al., 1994). Soil Cd may be associated with several geochemical phases such as clay minerals, organic matter, Al, Fe and Mn oxides, hydroxides and oxyhydroxides, carbonates, and sulfides. The degree of Cd association with these soil components is strongly dependent upon soil pH, the redox conditions prevailing, the extent of organic matter degradation, and grain size distribution (He and Singh, 1993a). At the lowest degree of association of Cd with soil components, the easily soluble or exchangeable forms are obtained. At higher degrees of the association, Cd is strongly bound to inorganic phases like clay minerals, oxides, hydroxides, oxyhydroxides and organic matter. Under high pH, strong associations of Cd with soil components and co-precipitates are formed. At higher degrees of the association, Cd availability or mobility may be substantially lowered, and it may be elevated at lower degrees of the association. Most studies involving Cd have been limited to soils of the temperate regions where the greatest proportion of soils is dominated by permanently charged surfaces having a net negative charge. In contrast, the retention of Cd by the strongly weathered tropical soils depends on soil environmental factors such as pH determined by management practices (e.g., liming), ionic strength of the soil solution, the presence inorganic and organic ligands etc., which play important roles in determining

surface properties of these soils (Naidu et al., 1997). The chemical forms or species are important in determining the mobility and bioavailability of the Cd in the soil environment (Holm et al., 1995). The distribution of Cd among various chemical forms can be measured by sequential extraction technique (e.g., Krishnamurti et al., 1995a). According to Alloway (1995), the mobility and bioavailability of Cd is influenced by its speciation, adsorption or coprecipitation onto hydrous metal oxides and complexation with organic components of the root exudates and microbial metabolites. An understanding of Cd transformations and kinetics of its release from the soils in the presence of various organic and inorganic ligands is essential for assessing the bioavailability of Cd in the environment.

Low-molecular-weight organic acids (LMWOAs) are common in soil solution (Fox and Comeford, 1990). Organic acids are nonhumified substances that may be released into the soil environment by decay of plant, animal and microbial tissues (Tan, 1986). In the immediate vicinity of plant roots the concentration of LMWOAs can be much higher than millimolar due to root exudates and to microbial processes (Robert and Berthelin, 1986). The importance of the formation of metal-organic acid complexes in increasing the solubility of trace elements in the rhizosphere has been reported by Merckx et al. (1986) and Mench et al. (1988). Low-molecular-weight organic acids secreted by plant roots modify the mobility of Cd through the formation of soluble complexes in the soil rhizosphere. Hence the kinetics of Cd release from soils as influenced by low-molecular-weight organic acids and its impact on Cd bioaccumulation warrant in-depth studies.

The influence of anions on Cd sorption has been studied by a number of groups (Garcia-Miragaya and Page, 1976; Sakurai and Huang, 1996). Chloride generally reduces Cd sorption by soil and has been identified as increasing the mobility of Cd through soils (Garcia-Marigaya and Page, 1976; Egozy, 1980; Boekhold et al., 1993). This is attributed largely to the formation of Cd-chloride complexes. The ionic strength of the solution and

the presence of competing cations are also known to affect Cd sorption in soils (Boekhold et al., 1993; Naidu et al., 1994a; Sakurai and Huang, 1996). The application of KCl fertilizer (muriate of potash) to tropical soils to supplement the soil supply of K, and to avoid soil depletion of K could enhance Cd release from these soils. The effect of high concentrations of Cl ions on Cd dynamics should be especially noteworthy in the fertilizer granule-soil interface. To date, the information on the kinetics of Cd release from tropical soils by KCl is not available in the literature.

Phosphate fertilizers applied to tropical soils to correct phosphorus deficiency can lead to various interactions of phosphate with soil components. The formation of phosphate-reaction products in soils with high contents of Al and Fe oxides has been suggested by Prabhudesai and Kadrekar (1984). The release of concentrated P into the surrounding soil alters the composition of soil solution and this results in the release of some cations due to dissolution (Lindsay et al., 1962). The phosphate-induced K release from soils has been reported by Zhou and Huang (1995). However, phosphate-induced Cd release from tropical soils remains to be uncovered.

Despite the potential health hazard of Cd to human beings and its presence in the agricultural soils, little attention has been paid to the Cd speciation and dynamics in tropical soils. Hence the objectives of this study were to investigate (1) Cd status, speciation and the fate of applied Cd in selected tropical soils from Kenya and (2) the effect of soil properties, LMWOAs, and application of phosphate and KCl fertilizers on the kinetics of Cd in the soils.

2. LITERATURE REVIEW

2.1 Cadmium in the Environment

2.1.1 Sources and distribution of cadmium in the environment

Cadmium is a relatively rare natural element that is widely dispersed in the earth's crust at concentrations generally below 1 mg kg^{-1} (Wakita and Schmitt, 1970; Bailey et al., 1995). It does not exist in concentrations sufficiently high enough to justify mining but is present in zinc ores from which it is extracted. It was discovered in 1817 as a constituent of Smithsonite ($ZnCO_3$) obtained from a zinc ore by a German Chemist F. Strohmeyer (Page and Bingham, 1973). Cadmium is also associated with phosphate rocks used in the manufacture of phosphate fertilizers. Cadmium is obtained as a by-product from the smelting of sulfide ore minerals in which it has substituted for some of the zinc. The most abundant sources of Cd are ZnS minerals sphalarite and wurtzite and secondary minerals, such as $ZnCO_3$ (Smithsonite) which typically contain 2-4 g Cd kg^{-1} although concentrations of up to 5 g Cd kg^{-1} can be found (Alloway, 1995). The concentration of Cd in these ores is usually related to the zinc content and increases as the content of zinc increases. Page and Bingham (1973) suggest that soils derived from igneous rocks would have Cd contents of 0.1-0.3 mg Cd kg^{-1} soil , those on metamorphic rocks would contain 0.1-1.0 mg Cd kg^{-1} soil and those derived from sedimentary rocks 0.3-11 mg Cd kg^{-1} soil. The Cd content of rocks is presented in Table 2.1.1.

There are two main sources of Cd in the environment, namely natural and anthropogenic. Cadmium chemical compounds are naturally present in zinc, copper and lead minerals and in certain phosphate rocks. There is a close relationship between the Cd

content of the soil and the parent material from which the soil developed during weathering. In mineral soils, background concentrations of Cd are in the range 0.1 to 0.4 mg kg^{-1} soil and can be as high as 4.5 mg kg^{-1} in volcanic soils (Bailey et al., 1995).

Table 2.1.1 Cadmium concentrations in rocks (Alloway, 1995)

Rock/Mineral	Range	Mean
	mg kg^{-1}	
Igneous rocks		
Rhyolites	0.03 - 0..57	0.23
Granites	0.01 - 1.60	0.20
Basalts	0.01 - 0.60	0.13
Metamorphic rocks		
Gneisses	0.007 - 0.26	0.04
Schists	0.005 - 0.87	0.02
Sedimentary rocks		
Shales and clays	0.017 - 11	
Black shales	0.30 - 219.0	
Sandstones and conglomerates	0.019 - 0.4	
Carbonates	0.007 - 12	
Phosphorites	< 10 - 980	
Sulphide ore minerals		
Sphalerite (ZnS)	0.2 - 0.4	
Galena (PbS)	< 5	
Tetrahedrite-tennartite (Cu, Zn)(Sb, As)S	0.24	
Metacinnabar (HgS)	< 117	

The levels of Cd in soil have been shown to decrease with increasing depth as Cd tends to accumulate on top soil together with humus due to cycling through vegetation (Andersson, 1977; Alloway, 1990). Apart from the fact that the surface horizon is the zone of highest organic matter content, many metals may be retained in this strongly adsorptive horizon after reaching it as a result of cycling through vegetation, or from applications of Cd containing fertilizers and manures, or from wet and dry deposition from the atmosphere (Alloway, 1995).

Anthropogenic Cd agents are major contaminating sources of soils and may exceed input from natural sources by two fold or more (Alloway, 1995). The sources of Cd to soils are either primary sources such as fertilizers, amendments and sewage sludge or secondary sources where Cd is added to the soils as a consequence of mining and metallurgical industries, forest fires and volcanic activities. Cadmium pollution of the environment has been rapidly increasing in recent decades as a result of rising consumption of Cd by industry.

Sewage sludge, manures and phosphate fertilizers are the important anthropogenic sources of Cd to agricultural soils. In most countries where extreme cases of Cd contamination of soils has been reported, the source of contamination has been traced to the use of sewage sludge (Bailey et al., 1995). It is estimated that 42 % of the 5.6 million tonnes/yr of sludge produced in the USA is applied to agricultural land and a similar percentage of the 5.9 million tonnes/yr produced in western Europe is also applied to agricultural lands (Bailey et al., 1995). The Cd content of sewage sludge is highly variable due to the nature and volume of the effluents discharged in the sewers. Alloway (1995) reported concentrations ranging from 1 to 3650 mg Cd kg^{-1} (dry matter) in sludge from western Europe and North America. In Canada, values ranging between 0.3 to 236 mg Cd kg^{-1} have been reported in seven cities (Bailey et al., 1995). When sludge is added to soils, heavy metals appear to remain in the zone of application (0-15 cm depth) as a result of adsorption on hydrous oxides, clays and organic matter, the formation of

insoluble salts, or the presence of residual sludge particles. The Cd content of phosphate (P) fertilizers is dependent on the source of the phosphate rock. The levels of Cd in some rock phosphates is presented in Table 2.1.2.

Table 2.1.2 Cadmium content of some rock phosphates

Phosphate rock	Cd (mg kg^{-1})	Reference
USSR (Kola)	0.2	McLaughlin et al. (1996)
South Africa (Phalaborwa)	4	Williams (1974)
China (Yunan)	5	Syers et al. (1986)
Syria (Khneifiss)	5	Bramley (1990)
Jordan	6	Bramley (1990)
Australia (Duchess)	7	Williams (1974)
Mexico	8	Syers et al. (1986)
Tanzania (Minjingu)	9	Kpomblekou & Tabatabai (1994)
Florida (North)	10	Kpomblekou & Tabatabai (1994)
Florida (Central)	11	Kpomblekou & Tabatabai (1994)
Peru (Sechura)	11	Syers et al. (1986)
Israel (Arad)	12	Syers et al. (1986)
Morocco (Khouribga)	13	Kpomblekou & Tabatabai (1994)
Israel (Zin)	32	Bramley (1990)
North Carolina	42	Kpomblekou & Tabatabai (9194)
Christmas Island	43	David et al. (1978)
Togo (Hahotoe)	47	Kpomblekou & Tabatabai (1994)
Banaba (Ocean Island)	99	Williams (1974)
Nauru	100	Syers et al. (1986)
Western USA	60-340	Auer (1977)

Although high Cd contents in soils and plants may be partly due to high native Cd contents in soils or to airborne sources, several studies have reported an increase in the Cd content of plants and soils in the cultivated layer following application of high rates of phosphates (Kaarstad, 1991; Mortvedt, et al., 1981; Mulla, et al. 1980; Williams and David, 1976). The accumulation of Cd in soils from long-term application of P-fertilizers is well documented (Tiller et al., 1995; Chaney and Hornick, 1978). This is the result of the presence in phosphatic rock ore of varying concentrations of several heavy metals, including Cd, which are not eliminated during manufacture of phosphatic fertilizer. But, when P-fertilizers are used, the increase in soil Cd concentrations is much smaller as compared to sludge application.

The contribution of manure to the Cd content of soils is two fold, (i) the Cd content of the manure and (ii) the apparent ability of the manure to mobilize soil Cd, making it more available to plants. On dry weight basis, farm yard manures contain on average 0.3 to 1.8 mg kg^{-1} Cd (McGrath, 1984; Kabata-Pendias and Pendias, 1992). Manures are believed to mobilize Cd due to high nitrogen content and organic acids of the manures which lower the soil pH, thus mobilizing Cd. The organic acids may also provide binding sites for the Cd^{2+} from where it can enter the soil solution and become available to plants.

The Cd content of typical agricultural soils is in the range of 0.1 to 0.4 mg kg^{-1} (dry weight). But, in contaminated soils the values can range from 6 to 97 mg kg^{-1} with maximum concentrations being as high as 600 mg Cd kg^{-1} . The European Economic Community (EEC) standard for agricultural soils is 1 to 3 mg Cd kg^{-1} soil, but in some soils of the EEC countries, mean values of 1 to 10 mg kg^{-1} have been reported.

Cadmium contribution to agricultural soils from mining and processing of non-ferrous metals, and from atmospheric deposition is only of significance in or near regions where metallurgical industries are prevalent. The impact of smelting activities on metal contamination of soils is well documented (Lagerwerff and Specht 1970; Buchauer, 1973;

Hutchinson and Whitby, 1973). In a study conducted by Sillanpaa and Jansson (1992) on Cd status of thirty countries, it was observed that soils from more industrialized countries had higher levels of soil Cd, which was a reflection of industrial activities in those countries. In Europe, it is estimated that Cd from atmospheric deposition is higher than in the USA; in the USA estimates of deposition per kg soil per year are: < 0.089 μg for rural areas, 0.98 μg metropolitan areas and 29 mg for industrial areas (Sposito and Page, 1984). Depending on the source of P-fertilizer, sewage sludge, manures, industrial activities and the emission from point source, the input of Cd to soils is quite variable.

2.1.2 Cadmium toxicity and its effects on ecosystem health

The potential for contamination of the food chain by Cd through bioacummulation in plants has recently received increased attention. Although Cd is not essential for plant growth (Kabata-Pendias and Pendias, 1992), it is readily taken up and accumulated by plants in appreciable quantities. Cadmium is a very toxic metal present in soils and has been responsible for a number of health problems. Animals are more sensitive to Cd than are plants; therefore, plants may accumulate Cd to levels of toxicological concern without evidence of phytotoxicity (Wolt, 1994). The dramatic effect of Cd is the development of *Itai Itai* disease where the outcome is osteomalacia, which is a softening of the bones, usually produced by Cd-induced deficiency of vitamin D. Further, it was reported that ingested Cd causes kidney dysfunction (Kobayashi, 1978; Tsuchiya, 1978; Friberg et al., 1985). The carcinogenic effect of Cd has been established, especially lung cancer (Kazantzis et al., 1992). It has been reported that exposure to Cd could contribute to the development of cancer of the prostate (Kazantzis et al., 1992); however, from the current epidemiological studies, Cd does not appear to act as a prostate carcinogen (Kazantzis et al, 1992).

The joint FAO/WHO Expert Committee on Food Additives (JECFA), which deals with food contaminants has set a Provisional Tolerable Weekly Intake (PTWI) of

0.42 to 0.50 mg of Cd per person or 0.06 to 0.07 mg/d of Cd (Fox, 1988). The JECFA has noted that Cd has a long biological half-life in humans, 40 days in the blood and 20 years in the liver and kidney organs in which it accumulates. At present no sequestering agent capable of stimulating Cd excretion has been identified. The ingestion of Cd in the duodenum is governed by a number of factors, for example Ca deficiency, and inadequate supply of Fe and Zn in the diet have been shown to increase Cd ingestion. Cd competes with a number of elements (e.g., Zn, Cu, Fe, Ca, Se, Mn) resulting in their deficiency in the human body. The Cd ions are stored in the liver in the form of metallothionein-cadmium complex, and are transported as such by the blood to the kidneys where it is absorbed by the proximal tubule cells. Metallothionein is the main protein that Cd is associated with, and has a stoichiometry of seven cadmium atoms per protein molecule (Kotsonis and Klaassen, 1981; Kagi and Hapke, 1984; Otvos et al., 1989). Cadmium induces the synthesis of metallothionein in the liver. The metallothionein-Cd complex is then transported to the kidney where it is adsorbed by the proximal tubule cells (Fergusson, 1990). The acute effects of Cd may arise from the metal not being bound to the metallothionein, and chronic effects when the capacity of the metallothionein to bind Cd becomes exceeded (Fergusson, 1990). The Cd induces renal tubular dysfunctioning characterized by a greater elimination of proteins with low molecular weight, notably β_2-microglobuline (FAO/WHO, 1995). An accumulative intake of 2.0 mg Cd or more, can lead to irreversible nephropathy, and kidney failure (Friberg et al., 1985; FAO/WHO, 1995). At lower levels of nutritional deficiency, the ingestion of Cd in foods upsets the metabolism of Ca in bone tissue.

Food is the main route by which Cd enters the body, however, FAO/WHO (1995) approximates that the average intake of Cd from the atmosphere is in the order of 0.0002 mg/d, of which about 25 % is absorbed. In contrast, smoking a pack of 20 cigarettes daily can result in inhalation of 0.002 to 0.004 mg Cd/d, the amount varying according to the country of origin of the tobacco (based on soil bioavailable Cd). A

summary of the principal sites where Cd exhibits its toxic effect in human beings, and the resulting health effect is given in Table 2.1.3

Table 2.1.3 The health effects of cadmium on human beings (Fergusson, 1990)

Exposure	Site	Health effects	Comments
Acute	Lungs	Bronchitis, pneumonitis	Can be fatal
	Gastro-intestinal tract	Nausea, vomiting, abdominal pains, diarrhea, vertigo	Can be fatal
	Liver	Toxema	
Chronic	Lungs	Emphysema, cancer	
	Kidneys	Proteinuria, aminoaciduria, phosphaturia, glucosuria, Cd^{2+} in urine, kidney stones	Due to proximal tubule and glomerular dysfunction
	Bones	Intense pain, lumbar pains, pseudofracturing, osteomalacia	May also require vitamin D and nutrition deficiency
	Enzymes	Inactivate enzymes	Zn replaced by Cd
	Blood system	Hypertension	In animals
		Anemia	Cd competes with Fe

2.2 Status and Speciation of Cadmium in Soils

2.2.1 Properties of cadmium

Cadmium is element number 48, having atomic mass 112.4, density 8.6 g cm^{-3}, m.p. 320°C and b.p. 765°C. It belongs to group II B of the Periodic Table, and is a relatively rare metal, being 67th in order of elemental abundance (Alloway, 1995). It has eight stable isotopes in nature; ^{106}Cd, 1.22%; ^{108}Cd, 0.88%; ^{110}Cd, 12.39%; ^{111}Cd,

12.75%; ^{112}Cd, 24.07%; ^{113}Cd, 12.26%; ^{114}Cd, 28.86%; and ^{116}Cd, 7.58%. Cadmium is between Zn and Hg in the Periodic Table of elements. Cadmium and Zn, however, differ from Hg in that the later forms particularly strong Hg-C bonds (Adriano, 1986). The atomic structure of Cd shows that there are two valence electrons which are quite a distance from the nucleus, and are easily lost. As a result Cd shows only metallic properties, and in its compounds, it is divalent and its ion is colorless.

Cadmium is a soft, silvery white, ductile metal with a faint bluish tinge resembling zinc in appearance and behavior. It is slightly harder and heavier than zinc and is more malleable and ductile. It dissolves readily in nitric acid, but it requires heat to effect solution in hydrochloric and sulfuric acids. Cadmium vapor is very reactive, quickly forming finely divided cadmium oxide in air (Nriagu, 1980). Cadmium is not affected by dry air but oxidized readily in moist air with the formation of protective coating of oxides. Cadmium oxide varies in color from greenish yellow through brown to nearly black. The colors are as a result of various kinds of lattice defect (Cotton and Wilkinson, 1988). Unlike zinc, Cd does not dissolve in bases (Cotton and Wilkinson, 1988). It forms strong complexes with cyanides and amines; many σ-bonded organometallic compounds of Cd have been synthesized under catalytic reactions (Aylet, 1979).

Cadmium has a stronger affinity for sulfur than zinc, and exhibits a higher mobility than zinc in acidic environments. Under conditions of strong oxidation, Cd is likely to form minerals (CdO, $CdCO_3$) and is likely to accumulate in phosphate deposits (Kabata-Pendias and Pendias, 1992). Cadmium ions form insoluble white compounds, usually hydrated, with carbonates, arsenates, phosphates, oxalates, and ferrocyanides.

2.2.2 Speciation of cadmium in soil solution

In order to understand fully the dynamics of the metal in agricultural and natural ecosystems, it is important to identify the forms (*species*) of metals in the soil, especially in the soil solution. Trace metals may be distributed among many components of the soil

or sediment and may be associated with them in different ways. The nature of this association has often been referred to as *speciation*. The knowledge of total Cd content of soils does not correlate well with biological availability and gives no information on the chemical reactivity of the different forms of the metal found in soils (Spevackova and Kucera, 1989). It is the chemical *species* or *form* that determines the mobility and bioavailability of the soil metals to other environmental compartments (such as water, plants, and biota) when physicochemical conditions are favorable. Much evidence indicates that the uptake of Cd by plants may be related to its chemical forms rather than total concentration in solution (Allen, et al., 1980; Bingham et al., 1984,1986). Free Cd (Cd^{2+}) is probably the Cd form most available to plants (Sposito et al., 1982).

The soil solution plays a critical role in controlling the availability of ions to plants. But the solubility and therefore the bioavailability of Cd is variable because many factors affect its concentration in soil solution (Lorenz et al., 1994). Soil solution is the central focus of soil chemistry since it is from this medium that plants absorb nutrients and it is the center of all important soil chemical processes (Lindsay, 1979).

The toxic effect of a metal is determined more by its form than by its concentration. The free Cd^{2+} is more likely to be adsorbed on the surface of soil solids than other species, such as the neutral or anionic species. During weathering Cd goes readily into solution. The principal species of Cd in the soil solution is Cd^{2+} but the metal may also form several complex ions, e.g., $CdCl^{+}$, $CdOH^{+}$, $CdHCO_3^{+}$, $CdCl_3^{-}$, $CdCl_4^{2-}$, together with organic complexes (Kabata-Pendias and Pendias, 1992). Hyroxides of Cd are formed when solutions of Cd salt are added to bases (Aylet, 1979; Cotton and Wilkinson, 1988). The concentration and speciation of a metal such as Cd in the soil solution will depend partly on the concentration of ligands in the soil solution and the stability constants of the metal-ligand complexes.

Attempts to determine the species of Cd and other trace metals in soil solutions include separation methods such as dialysis, ultrafiltration, centrifugation, separation on

ion exchange resins and gel filtration (Tills and Alloway, 1983). These methods, however, suffer from poor resolution between species and uncertainty with regard to the recovered chemical form. Electrochemical methods using ion selective electrodes or polarographic analyses are not reliable enough at the very low concentration range ($<10^{-7}$ M) typical for Cd in soil solutions (McBride, 1980; Street et al., 1977). Differential pulse anodic stripping voltammetry (DP-ASV) measures the free Cd ion in solution and that associated with labile complexes, but not large organic Cd complexes. Thus, the direct determination of Cd species is confronted by experimental difficulties and uncertainties.

Several models are available for the prediction of the species present in aquatic systems. GEOCHEM was developed by Mattigod and Sposito (1979) specifically for soils. The model contains a database with typical values of stability constants for individual metal-ligand pairs. The insertion of parameters such as pH, organic C, cation and anion concentrations enables a prediction of the predominant species to be made. With the help of this model it has been predicted that the principal chemical species of Cd in oxic soil solutions are (in decreasing order): Cd^{2+} , $CdSO_4^o$ and $CdCl_4^{2-}$ in acidic soils, and Cd^{2+}, $CdCl^+$, $CdSO_4^o$ and $CdHCO_3^+$ in alkaline soils (Sposito and Page, 1984). Computer models (Parker et al., 1987; Parker, 1991) have been used to predict the species present in soil solutions.

However, some authors have found that predictions by GEOCHEM for the free-ion contents of some metals in soil solutions were not in close agreement with those determined experimentally. A new version of the GEOCHEM called the SOILCHEM has been developed (Sposito and Coves, 1988) and many of the problems encountered with GEOCHEM have been overcome (Alloway, 1995).

2.2.3 Speciation of particulate-bound cadmium of soil

Soils are complex media with solid, liquid and gaseous phases. The solid phase is composed of inorganic and organic matter, and living organisms. Much of the trace

elements associated with the solid phase are not available for plant uptake (Shuman, 1991). In fact, < 10% generally are in soluble and exchangeable forms (Lake et al., 1984). However in soil systems, an equilibrium exists between metals associated with solid phase and soluble metal species in soil solution. Because the concentrations of metals in soil solution are normally much lower than in solid phase, it is generally assumed that the solid phase buffers the activities of the ionic metals in soil solution (Chekai et al., 1987).

The pools of trace metals in soils associated with solid phase include exchangeable, adsorbed, organic-bound, hydrous oxide segment, and lattice component (Pickering, 1981). Charged metal ions in soil solution are adsorbed on charged surfaces of colloids. The prevalent colloids are the layer alumino-silicates, hydrous oxides of Al, Fe and Mn, and solid organic matter. Exchangeable and adsorbed ions usually are grouped as one pool and are extracted together, although some schemes make distinctions between weakly adsorbed (nonspecific sites) and strongly held ions (specific sites).

Oxides of Fe and Mn occur in soils as coatings or as concretions and as discrete particles of colloidal dimensions, and have a strong affinity for metal ions (Chao and Theobald, 1976). In calcareous soils metals can also be associated with carbonates (Shuman, 1991). Manganese oxides are less abundant than Fe oxides, but they exhibit a greater chemical reactivity and are present in many chemical forms (Chao and Theobald, 1976). Thus, trace metal concentrations are often high in the Mn oxides (Taylor and McKenzie, 1966). A majority of trace metals are found in the crystal structure of highly resistant primary and secondary minerals, which comprise the residual fraction after all other forms have been removed (Shuman, 1985).

An experimental approach commonly used to study the different chemical forms or *species* associated with solid phase in soils is selective sequential chemical extraction. Several soil and sediment selective sequential extraction schemes have been described in the literature (Gupta and Chen, 1975; Tessier et al., 1979; Shuman, 1983; Shuman, 1985;

Ramos et al., 1994; Krishnamurti et al., 1995a). Generally, these schemes use a sequence of reagents of increasing reactivity in the dissolution process. These methods do not provide a direct characterization of metal speciation, but rather an indication of chemical reactivity. The metal extracted may be associated with a specific chemical pool, the assignment of which is based on the extraction of pure chemical substances during method development. The reagents provide a means of estimating potentially available metal concentration (Martin et al., 1987; Kheboian and Bauer, 1987).

Depending on physicochemical characteristics of the soil, the nature, and concentration of the elements, deviations between results obtained by different sequential extraction schemes may be considerable. The problems found by several authors (Shuman, 1985; Kheboian and Bauer, 1987; Pickering, 1986; Rauret et al., 1989), independent of the speciation scheme used to obtain different fractions, were mainly related to three causes: (i) the limited selectivity of extractants; (ii) trace element redistribution among phases during extraction, and (iii) overload of the chemical system if the content of metal is too high.

The sequential extraction procedure used extensively by various environmental researchers for speciation of particulate-bound heavy metals in soils is that of Tessier et al. (1979). Recently, Krishnamurti et al. (1995a) developed a sequential extraction scheme for the speciation of particulate-bound Cd species of soils. Delineating the different forms of particulate-bound Cd of soils should be useful to identify the species important in controlling the bioavailability of Cd in soils and hence its toxicity.

2.2.4 Bioavailable cadmium of soils

In noncontaminated, noncultivated soils, Cd concentration is largely governed by the amount of Cd in the parent material. Reliable methods are available for the determination of total soil Cd, for example the HF-$HClO_4$ digestion method of Jackson (1958) and the microwave digestion method of Krishnamurti et al. (1994). The total

amount of Cd present in soil is one of the factors affecting the Cd contents of plant, however total soil Cd does not correlate well with the plant-available fraction (John et al., 1972).

Several chemical extractants have been tested to provide an index of plant available Cd. These include week acids, neutral salts, and chelating agents. Typical examples of extractants which have been used to measure plant-available Cd in soil are: HCl (Wear and Evans, 1968), ethylene diamine tetraacetic acid (EDTA) (Trierweiler and Lindsay, 1969), diethylene triamine pentaacetic acid (DTPA) (Lindsay and Norvell, 1978), ammonium oxalate (John et al., 1972), ammonium acetate acetic acid-ethylene diamine tetraacetic acid (AAAc-EDTA) (Lakanen and Ervio, 1971), ammonium hydrogen carbonate-diethylene triamine pentaacetic acid (AB-DTPA) (Soltanpour and Schwab, 1977), $CaCl_2$ (Jackson and Alloway, 1991) and NH_4Cl (Krishnamurti et al., 1995b). Because the efficiency and predictability of a given extractant can be strongly influenced by soil and plant factors, there is no universal extractant for Cd.

Chemical extraction methods typically quantify Cd by graphite furnace atomic absorption spectroscopy (GFAAS) which measures total Cd in solution. Differential pulse anodic stripping voltammetry (DP-ASV) offers an alternative low cost technique that measures only free metal ion and that associated with complexes which dissociate under the time scale of the experiment (Florence et al., 1986). DP-ASV may be expected to measure the Cd fraction which is more closely related to that taken up by plants since studies in natural waters have shown that the metal fraction measured by DP-ASV method is a good estimate of that fraction which is toxic to biota (Florence et al., 1986). Also it has been shown that the most readily plant-available forms of Cd are free metal ion and the exchangeable fraction; some organically-bound Cd species are not plant-available (Tyler and McBride, 1982; Chekai et al., 1987; Logan and Traina, 1993).

Plant uptake of trace metals is related to the metal activity in soil solution and to the ability of the solid phases to resupply the solution with those cations. Once the extractant

is added to the soil solution, it forms stable soluble complex or chelate with the metal ions. The binding strength of a chelate for a metal cation depends on the stability constant of the metal chelate complex. The higher the stability constant, the stronger the metal-chelate complex is. As the free metal ions are removed from solution through this complexation (or through plant root uptake), labile solid phases dissolve or surface cations desorb to replenish those in solution.

All forms of Cd do not have an equal bioavailability (Gunn et al., 1988). Hence, there is a need to determine a suitable soil test that would relate soil Cd to Cd uptake by plants in a range of soils. Such a test will be useful in identifying farms that have a potential Cd problem.

2.2.5 Factors affecting cadmium bioavailability in soils

The soil chemical processes affecting the availability of Cd to plants are particularly important in considerations of the impact of soil contamination on human health. A number of soil factors affect the uptake of Cd by plants. The origin of Cd in the soil has been reported to affect its bioavailability (Lund et al., 1981). Several workers have reported that crops grown on soils spiked with salts take up more Cd than those grown on soils containing the equivalent amount of Cd from sewage sludge (Alloway, 1985; Korcak and Fanning, 1985). Besides the addition of fertilizers, manures and other amendments, soil pH is most important (Sanders et al., 1986; Chang et al., 1987; Anderson and Christensen, 1988; Basta and Tabatabai, 1992a), so are clay content (Herms and Brummer, 1984), oxides of Mn and Fe (King, 1988), ionic interactions (Basta and Tabatabai, 1992b) and redox potential (Bingham et al., 1976; Reddy and Patrick, 1977).

Soil pH is often regarded as the major variable controlling the bioavailability of Cd in the soil (Chaney and Hornick, 1978). Increasing acidity (reducing pH) in solution culture has, however, been found to depress Cd uptake by plants, due to competition

between H^+ and Cd^{2+} for uptake (Tyler and McBride, 1982; Hatch et al., 1988). The pH effects on Cd availability in soils are largely due to the effect of pH on the retention of Cd^{2+} by soil surfaces. Field data on effects of liming on natural agricultural soils showed that plant Cd concentrations were negatively correlated with the soil pH (Eriksson, 1990; Sillanpaa and Jansson, 1992; He and Singh, 1993b).

It has been reported that the Cd content of plants was inversely proportional to the cation exchange capacity (CEC) of the soils on which they were grown (Hinesly et al., 1982; John et al., 1972; Miller et al., 1976). Organic matter contributes part of the soil's CEC but adsorbs heavy metals by forming complexes. However, the relationship between CEC and plant uptake remains unclear because cation exchange is only one of several adsorption mechanisms affecting solubility of Cd in soils.

Soil micronutrient status, particularly Zn, is another important factor that controls Cd accumulation by plants. Oliver et al. (1994) demonstrated that treatment of Zn deficiency or near-deficiency in field wheat crops by the application of small amounts of Zn (< 10 kg Zn/ha) significantly reduced grain Cd concentrations. The mechanism responsible for this reduction has not been determined, but may be related to the loss of root membrane integrity where plants are Zn deficient.

Soil salinity has been shown to control Cd accumulation by potato crops in Australia (McLaughlin et al., 1994). Soil salinization can be caused by either additions of chloride or sulfate salts in irrigation waters, or by the rise to the surface of these salts in groundwaters (dry land salinization). The presence of chloride in high concentrations in soil solution can lead to significant complexation with Cd, which reduces Cd sorption and increases total Cd concentrations in soil solution. Concentrations of Cl above about 10 mM lead to over 50% of the inorganic Cd in solution being chloro-complexed (McLaughlin et al., 1996). Sulfate salinity has been reported to have little impact on plant Cd uptake in both acidic and limed soils (Bingham et al., 1986).

Other factors identified as affecting Cd bioavailability of soils include: temperature (Giordano et al., 1979; Tiller, 1988; Hooda and Alloway, 1993) and addition of macronutrients P, K and N (John et al., 1972; Miller et al., 1976; McClean, 1976; Williams and David, 1976; Willaert and Veloo, 1992). Williams and David (1976) found that wheat crops fertilized with superphosphate and ammonium nitrate accumulated more Cd than crops fertilized with single superphosphate only. Levi-Minzi and Petruzzelli (1984) reported that the alkaline reaction products of diammonium phosphate (DAP) dissolution increased Cd retention by soil compared with monoammonium phosphate (MAP). Andersson (1976) reported that high concentrations of all soluble salts in the vicinity of the granules of most fertilizer types may be expected to increase Cd concentrations in soil solution through competitive cation exchange.

2.2.6 Cadmium speciation and cadmium availability index of soils

The speciation or chemical form of metal contaminants (e.g., Cd) is recognized to be of primary importance in determining their relative mobility, bioavailability, and ultimate impact on ecosystem health. Based on experimental conditions, extraction procedures have been developed which sequentially separate particulate-bound Cd species (Tessier et al., 1979; Krishnamurti et al., 1995a). All forms of Cd do not have an equal bioavailability (Gunn et al. 1988). Amounts of Cd extracted by reagents like ABDTPA (Soltanpour, 1991), AAAc-EDTA (Sillanpaa and Jansson, 1992) and NH_4Cl (Krishnamurti et al., 1995b) have been shown to correlate well with the plant-available Cd. The amount of extractable trace metal, which correlates well with the plant-available metal, is usually taken as the availability index of the metal for the soil.

Attempts have been made to correlate Cd availability index with the individual Cd species. Krishnamurti et al. (1995a), using the ABDTPA-extractable Cd as cadmium availability index of some Saskatchewan soils, observed a significant correlation between metal-organic complex bound-Cd species and cadmium availability index which indicated

that metal-organic complex bound-Cd was important in influencing Cd availability in these soils. The formation of metal-organic complexes has been proposed to be the general mechanism for the accumulation of heavy metal ions in plant vacuoles (Rauser, 1990; Woolhouse, 1983; Krotz et al., 1989; Vogeli-Lange and Wagner, 1990).

ABDTPA-extractable Cd (Soltanpour, 1991) reflects well the plant-available Cd of neutral and calcareous soils and can be used as Cd availability index (CAI) for such soils. The use of ABDTPA-extractable Cd as the Cd availability index for calcareous soils has also been reported by Krishnamurti et al. (1995a). The AAAc-EDTA extraction method developed by Lakanen and Ervio (1971) for the determination of plant-available Cd and other trace metals has been shown to correlate well with plant available Cd (Sillanpaa and Jansson, 1992) especially for acidic soils. It is currently being used by the European Research Network on Trace Elements (Sillanpaa and Jansson, 1992). The AAAc-EDTA-extractable-Cd can therefore be used as Cd availability index of acidic soils. Recently, Krishnamurti et al. (1995b) showed that NH_4Cl-extractable Cd significantly correlated with the Cd accumulated in the grain of durum wheat cultivars and therefore suggested its use as Cd availability index for neutral and calcareous soils. The value of the stability constant of Cd-chloride complex (Smith and Martell, 1976) has a similar order of magnitude as that of Cd-organic acid complexes (Sillen and Martell, 1964) of many low-molecular-weight organic acids.

2.3 Transformations and Dynamics of Cadmium Introduced to Soils

2.3.1 Dynamics and equilibria of cadmium transformations in soils

Cadmium in soils can be associated with several distinct geochemical phases. Cadmium, like other trace elements is distributed within the soil system among seven major pools as presented in Figure 2.3.1 (modified from Peterson and Alloway, 1979). The pools are:

(a) the soil solution (elements as free ions or soluble complexes)

(b) the colloidal phase (elements as adsorbed ions; "the cation exchange complex")

(c) hydrous oxides of manganese, iron and aluminum (ions adsorbed and bound)

(d) soil organic matter (insoluble metal-organic complexes)

(e) solid phase-insoluble precipitates (e.g., sulfides, phosphates and carbonates)

(f) solid phase-minerals

(g) microorganisms and fauna

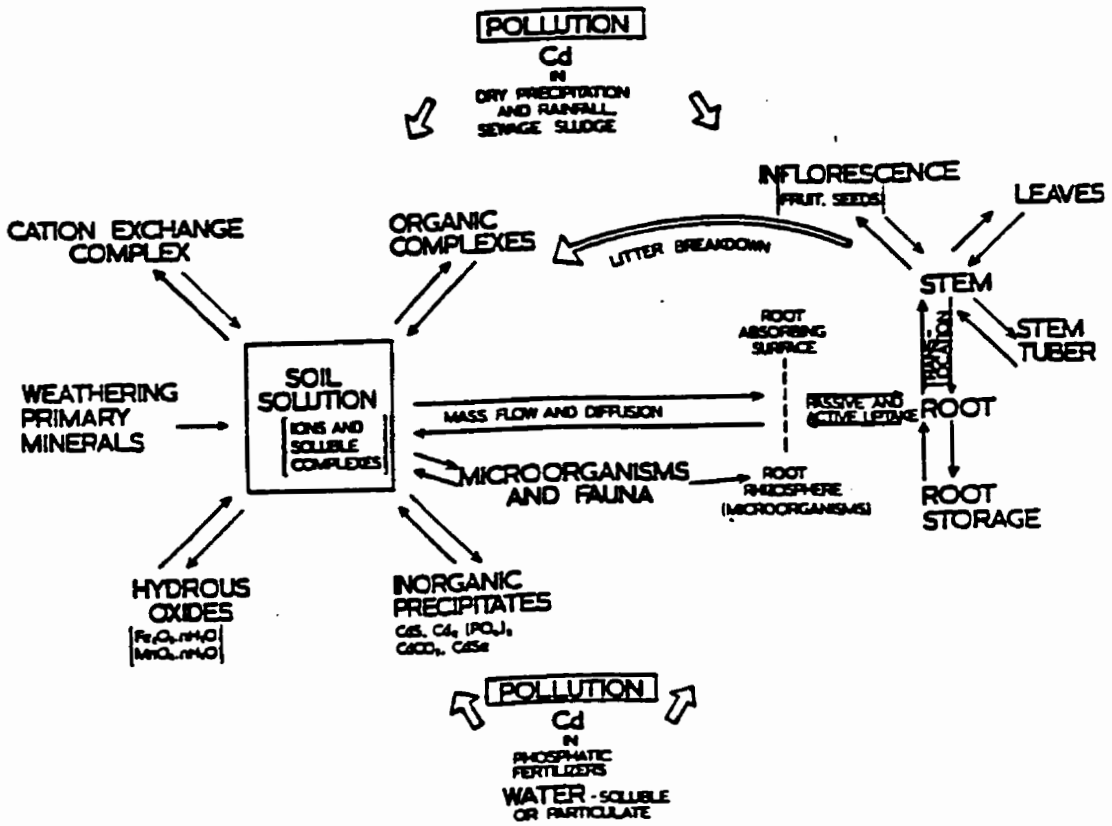

Figure 2.3.1 Cadmium in the soil-plant system (modified from Peterson and Alloway, 1979).

Only the Cd in soil solution is immediately available to plants. Hence, factors which control the distribution of Cd in the soil system effectively control the concentrations of Cd in the soil solution and thus the amount available for plant uptake (Perterson and Alloway, 1979). The pool of biologically active Cd (i.e., Cd^{2+}) can be reduced significantly by complexation reactions. The complexes of greatest importance are those with soft bases, as Cd^{2+} is a soft acid (Wolt, 1994). Cadmium being a soft acid would react and form complexes most readily with soft Lewis bases. Thus, complexation equilibria with inorganic ligands such as Cl^- and with certain types of organic ligands may be important.

Under conditions of strong oxidation, Cd forms oxidized minerals such as CdO and $CdCO_3$ (Goldschmidt, 1958). Following the release of Cd into soil solution, Cd^{2+} is rapidly partitioned between the mineral, organic and solution phases (McLaughlin et al., 1996). In solution, Cd^{2+}, like some of the other metal ions such as Zn^{2+}, is associated with a sheath of water molecules as presented below:

$$Cd(H_2O)_6^{2+}{}_{(aq)} \Leftrightarrow Cd(H_2O)_5(OH)^+{}_{(aq)} + H^+ \quad (pK_1 = 10.1) \text{ (Lindsay, 1979).}$$

Cadmium can also be present in soil solution in association with other ligands, namely, Cl^-, SO_4^{2-}, HCO_3^- or organic ligands in the form of complexes (Tills and Alloway, 1983). Table 2.3.1 shows stability constants of Cd with selected inorganic anions .

In soil, Cd may be adsorbed onto exchange sites on clays, hydrous oxides and organic matter (Sposito and Page, 1984) or it may be specifically adsorbed by oxides and hydroxides of Fe, Al and Mn (Tiller et al., 1984). The mechanisms involved in the retention of Cd^{2+} by iron and manganese oxide minerals, silicate clay minerals and whole soils have been investigated; the studies reveal that Cd may be retained through both precipitation and sorption processes (Brummer et al., 1988). The precipitation of Cd

occurs mainly under conditions of high anion concentrations and at high pH, although CdS can form under acidic reducing conditions.

Table 2.3.1 Stability constants of Cd with selected inorganic anions (Smith and Martell, 1976; Dean, 1992)

Ligand	Complex	log K
Cl^-	$CdCl^+$	1.98
	$CdCl_2^o$	2.50
	$CdCl_3^-$	2.60
	$CdCl_4^{2-}$	2.80
SO_4^{2-}	$CdSO_4^o$	2.45
NO_3^-	$CdNO_3^+$	0.50
	$Cd(NO_3)_2^o$	0.20

The reactions of Cd with each soil component will depend on a number of factors, e.g., soil type, pH, rainfall, temperature, time, management practices and the source of applied Cd. Cadmium may associate with ammonium ions to form $Cd(NH_3)^{2+}$, but this is only likely to form in the vicinity of dissolving diammonium hydrogen phosphate (diammonium phosphate, DAP) fertilizer granules, where the pH and NH_3 concentrations may be high (Lindsay, 1979). Interactions between Cd and other metal ions, e.g., zinc have also important implications on its biogeochemistry. Competition for binding and exchange sites within the soil itself increases Cd extractability from the soil, and the resulting Cd concentrations in soil solution, when Zn concentration in soil is increased.

The fate of Cd introduced to soils will be controlled by a complex set of chemical reactions and by a number of physical and biological processes acting within the soil. The initial mobility after addition to soils will largely depend on the form in which it is added; this in turn, depends on its source (Jones and Jarvis, 1981). It has also been reported that

the specific chemistry and fate of heavy metals in soils are affected by formation of stable complexes with soil organic compounds (Schnitzer, 1978; Berthelin et al., 1995).

Many investigators have demonstrated that the ease of extraction of applied elements in soils becomes increasingly difficult with increasing periods of reaction. The increased retention of added metal ions has been attributed to reactions within the surface layer or inside the structure of minerals. Studies by Brummer et al. (1988) show that Cd may be entrapped following diffusion into goethite, Mn oxides and other minerals present in soils. Such a mechanism may be one of several processes that could explain why ions added to soils become increasingly difficult to desorb and become less available with time. In comparison with other metals, the rate at which Cd becomes firmly bound is not as great as for Zn and Ni (Christensen, 1984a,b; Brummer et al., 1988).

Regardless how Cd enters the soil system, the chemical and biological factors of the soil eventually control its uptake by plants and its mobility in soils. Over time, a Cd salt solution would react with the soil and convert Cd to less available and more insoluble forms (Bell et al., 1991). The Cd salt additions add only the counter anion associated with Cd, while additions like sludge add organic matter, soil minerals carried in the waste stream, and possibly Fe and lime added in the treatment process (Baldwin et al., 1983). Sludge constituents can also lower Cd^{2+} activity in the soil solution via complexing by soluble ligands or colloidal surfaces. Cadmium may also exist in mineral forms, such as precipitates, coprecipitates or occlusions in phyllosilicate and sesquioxide minerals (Rudd et al., 1984; Corey et al., 1987).

Cadmium added to soils has been reported to transform with time to less soluble forms; the extent depends upon the type of soil. The rate of transformation in a particular soil is affected by both pH and rate of Cd addition (Mann and Ritchie, 1994). The extent of Cd build-up in soils varies with the type of soil, Cd content in the fertilizers and the management practices involved (Mortvedt et al., 1981; Tiller et al., 1984; Alloway,

1990). The nature of interactions between Cd and the soil solid phase will, therefore, affect its mobility in soil.

The role of microorganisms in geochemical cycling of the major elements is relatively well understood on the global scale (Kabata-Pendias and Pendias, 1992). Soil microorganisms are able to act directly or indirectly on the dissolution or deposition processes of heavy metals by mechanisms that involve oxidation, reduction, acidification, complex formation, biosorption, and bioaccumulation (Berthelin et al., 1995). Microbial transformations can result in environmental pollution or detoxication processes. The physicochemical relationship between bacteria and mineral surfaces leads to diverse effects of dissolution and secondary precipitation of trace metal ions, including changes in their valence and/or conversion into organometallic compounds. Many bacterial species are involved in the transformation of trace metals, including even neoformation of certain Fe and Mn minerals. Bacteria also play an important role in gley formation which affects the mobility of metals in soils. Microbially induced decreases in the availability of trace elements result from a high accumulation of certain elements by microbiota and also from the biological oxidation of compounds of these elements. Microbiological increases of availability, on the other hand, are caused by microorganisms capable of reducing certain elements (principally, Mn and Fe). When energy sources are available, microorganisms solubilize heavy metals (e.g., Cd, Pb, and Cu) that were fixed or bound to soil mineral constituents or organic matter. Insolubilization of heavy metals can be associated with the biodegradation of the organic ligands of soluble metal-organic complexes (Munier-Lamy et al., 1991).

2.3.2 Sorption-desorption of Cadmium in soils

It has been suggested that trace metal concentrations in soil solutions are likely to be controlled by adsorption-desorption equilibria at low metal concentrations, while at higher metal concentrations, precipitation-dissolution reactions become important when

adsorption sites are limited (Brummer et al., 1983; Tiller et al., 1984). For most agricultural soils, therefore, with relatively low Cd loading, Cd^{2+} solubility is unlikely to be controlled by the dissolution of known Cd compounds (Lindsay, 1979), but rather by sorption-desorption reactions. The sorptive properties of a soil will determine the partitioning of Cd between the solid and liquid phases and therefore the potentially bioavailable pool of soil Cd.

Sorption processes can be separated broadly into two groups, depending on the affinity of the adsorbent for the adsorbates. When cations are bound by weak electrostatic forces simply to balance the negative charge on surfaces, the process is called non-specific sorption and the Cd ions adsorbed in this way are equivalent to the well defined exchangeable cations. These non-specifically sorbed Cd ions are easily replaced by ions from neutral salts such as NaCl, $CaCl_2$ (Sauerbeck and Styperek, 1984; MacLaughlin et al., 1996), NH_4NO_3 (Symeonides and McRae, 1977). In the second type of sorption, ions are bound much more tightly to the adsorbent surface. This process is termed specific sorption and the sorbed Cd ions are much less easily removed from the surface (Hodgson et al., 1964). It is generally accepted that the specific sorption of heavy metals by soil mineral increases with the hydrolysis of the metal ion (Hodgson et al., 1964; Forbes et al., 1976).

Cadmium sorption is described by most researchers by either the Langmuir equation or the Freundlich isotherm. Jarvis and Jones (1980) found that Cd adsorption at initial concentrations of 0.5 -100.0 μM was described by the Freundlich adsorption equation, but isotherm gradients were steeper when initial concentrations were < 0.5 μM, indicating the presence of specific sites of differing absorption energy. Two types of adsorption sites were suggested: (1) low-capacity, high-affinity sites at low solution concentrations of Cd, and (2) lower-affinity, but higher-capacity sites at higher solution Cd concentrations. Variations between soils in isotherm gradients at low initial Cd concentrations were largely accounted for by the free iron oxide contents.

Alloway (1995) reported that over a wide range of concentrations, adsorption was best described by the Freundlich isotherm, but the isotherms comprised of two linear sections. John (1972) found Cd adsorption data onto soil fitted the Langmuir isotherm. Soil sorption of Cd is a fast process; most of the sorption takes place within 10 minutes, and the equilibrium is reached within an hour (Christensen, 1984a; Sakurai and Huang, 1995). The findings by Christensen (1984a) suggest that soil sorbed Cd is not irreversibly bound; changes in the absolute composition with respect to Zn, $CaCl_2$, pH and the presence of EDTA caused significant release of previously sorbed Cd.

Variation in Cd sorption properties has been related to soil characteristics which may vary in different geographical regions. Jenne (1968) reported that the sorption potential for divalent metals is determined primarily by the quantities of soil organic matter and oxides of Fe and Mn present in the soil, because these phases have high affinity for metallic cations (Taylor and McKenzie, 1966). The primary role of layer silicates may be to provide a substrate on which amorphous Fe and Mn oxide precipitate, although recent results by Zachara et al. (1992) suggest that the charge on the layer silicates themselves may be the principal force driving sorption of Cd. The hydroxyaluminum-montmorillonite complex which is one of the major constituents in acidic soil environments has been shown to adsorb Cd rapidly and the reaction is virtually completed within 10 minutes (Sakurai and Huang, 1995).

Electrokinetic studies on clay suspensions have shown that, at pH values greater than 2 or 3, the particles carry a net negative charge (normally compensated for by the presence of positive counterions) (Pickering, 1980). The charge originates from lattice imperfections, exposed structural hydroxyl groups, broken bonds at edges of particles, and isomorphic substitution within the lattice. The first three sources predominate in kaolinite while in illites and montmorillonites most of the charge or exchange capacity is attributable to isomorphous substitution. The counterions which are present in the surface film of clays are not strongly bound and are therefore readily exchanged, for example,

$$\text{Clay-}Ca^{2+} + Cd^{2+} \Leftrightarrow \text{Clay-}Cd^{2+} + Ca^{2+}.$$

In acidic soils the reaction is largely reversible and at about pH 5.5 some of the heavy metals, notably Cd^{2+}, are not much stronger competitors than Ca^{2+} for adsorption by inorganic colloids. However, as the pH increases above 5.5 adsorption increases abruptly and with many of the metals the reaction becomes partly irreversible, i.e., the metal ion cannot be exchanged against, for example, NH_4^+ or Na^+ (Jones and Jarvis, 1981).

In addition to major soil properties, there are numerous factors that influence the dynamic equilibrium between Cd in the soil solution and the sorbed phase. Some of these factors include solution pH, ionic strength, competing effect of other cations, inorganic and organic ligands. The effect of these factors on Cd bioavailability were discussed in Section 2.2.5. The effects of pH on soil sorption of Cd are well-known and extensively documented. With increasing pH, there is a characteristic pH above which sorption of Cd increases rapidly (Garcia-Maragaya and Page, 1978; Tiller et al., 1979; Basta and Tabatabai, 1992a; Zachara et al., 1992; Naidu et al., 1994a). Christensen (1984a) found that the sorption capacity of soil in the pH range 4.0 - 7.7 increased 2-3 times for a pH increase of one unit. However, the effect of pH on Cd sorption has been shown to depend on Cd loading, the nature of the soil constituents and the Cd retention capacity of the soils.

The presence of divalent cations (e.g., Ca^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+} and Pb^{2+}) retards the sorption of Cd by soils due to competition between Cd and these metals (Christensen, 1987; Homann and Zasoski, 1987). The lower sorption of Cd by soils in the presence of Ca^{2+} has been attributed to the competition for sorption sites between Ca^{2+} and Cd^{2+} ions. Reports on calcium as a competitive ion in the soil solution are variable. The use of $CaCl_2$ as background electrolyte is of some concern due to complexation reactions between Cd and Cl ion. It has been shown that soils containing free $CaCO_3$ can sorb Cd and reduce Cd bioavailability (Alloway et al., 1988). Christensen (1984b) observed Zn in

the soil solution at concentrations much higher than Cd only slightly affected Cd binding, indicating that Zn is not a strong competitor.

The influence of anions on Cd sorption has been investigated by a number of researchers. Chloride generally reduces Cd sorption by soil and has been identified as increasing the mobility of Cd through soils (Garcia-Miragaya and Page, 1976; Doner, 1978; Boekhold et al., 1993). This is ascribed to chloro-complexation of Cd in solution (McLaughlin et al., 1994, 1996). The addition of phosphate to solution appears to enhance Cd retention by soil. This effect may be related to precipitation of $Cd_3(PO_4)_2$ if P is added to the same solution as the Cd ions, or is due to enhanced sorption as evidenced by increased Cd retention of soils pretreated with P where precipitation of Cd phosphates is not expected (Kuo and McNeal, 1984; Naidu et al., 1994b). The effects of SO_4^{2-} on Cd sorption are less clear as SO_4^{2-} itself is a sorbing species in many soils and sorbed SO_4^{2-} impacts a greater negative charge than Cl^- to the sorbing surface (Benjamin and Leckie, 1982; Gessa et al. 1984). The effects of SO_4^{2-} on Cd sorption will therefore depend on the nature of the sorbing surfaces present in soil (Naidu et al., 1994b). Complexation of Cd with certain organic ligands in the soil solution can have major effects on the amounts sorbed. Soluble organic anions can affect Cd sorption by reducing Cd^{2+} activities in solution and also change the affinity of the sorbing surface for Cd^{2+} (Elliot and Denney, 1982; Ram and Verloo, 1985; Neal and Sposito, 1986).

Cadmium is also bound by humified organic matter in the soil, as soluble or insoluble metal-organic complexes (Peterson and Alloway, 1979). In addition to the formation of complexes (usually chelates), colloidal organic matter comprises part of the cation exchange complex, which is involved in the adsorption of Cd. The high-molecular-weight insoluble complexes act as Cd sinks and hence control the available metal concentration in soil solution.

2.4 Ionic Factors Affecting Cadmium Release from Soils

The presence of inorganic and organic ions in soil solution plays an important role in the release or retention of Cd. The Cd release or retention will depend on the nature of the ions and the conditions prevailing in the environment.

2.4.1 Low-molecular-weight organic acids

Organic acids play a key role in influencing nutrient availability to plants by participating in ligand exchange reactions on mineral surfaces, by promoting mineral dissolution, and by metal solubilization-chelation reactions (Kwong and Huang, 1978; 1979; Hoffland et al., 1989; Fox et al., 1990). Complexation of Cd with certain low-molecular-weight organic acids (LMWOAs) in soil solution can influence the release of Cd from the soil surfaces. It has been reported that the mobility of trace metals depends on their speciation, which can be assessed using sequential selective extraction procedures (e.g., Tessier et al., 1979; Krishnamurti et al., 1995a). The release of root exudates may influence nutrient solubility and uptake indirectly through their effects on microbial activity, rhizosphere physical properties and root growth patterns, and directly by acidification, chelation, precipitation and oxidation-reduction reactions (Uren and Reisenauer, 1988).

Natural organic acids originate from root exudates, canopy drip, in the oxidative decay products of plant and animal residues, and in microbial metabolites (Hue, 1988; Amador et al., 1989; Huang, 1991). Anthropogenic activities are also important sources of organic acids in soils (Snell and Ettre, 1969; Morill et al., 1982; Liu and Bollag, 1985). The application of sewage sludge to agricultural soils is likely to result in high amounts of some organic acids. Hue (1988) found that soils amended with sewage sludge contained organic acids like succinic and acetic, some were in very high concentrations. Anthropogenic activities may be important local sources of acetic acid (Kawamura et al., 1985) which is added to the soil by wet deposition.

Low-molecular-weight organic acids are constantly being added to soils through natural vegetation, microbial metabolism, agricultural practices and anthropogenic activities. Seasonal variation in LMWOAs have been reported, for example, Spakhova and Spakhova (1970) observed that aliphatic LMWOAs in soils reached a maximum in the autumn, whereas the phenolics reached a maximum in summer when the microclimatic conditions for microbial activity are optimal (Kuiters and Denneman, 1987; Kuiters, 1990). Blank et al. (1994) reported that activities like bush fire increased the levels of acetic, formic and oxalic acids in the surface 5 cm of soil.

Low-molecular-weight-organic acids in soil environments can be divided into aromatic and aliphatic organic acids (non-volatile and volatile) and amino acids (Stevenson, 1967). Generally, the relative abundance of these acids would follow the order: Volatile aliphatic acids, viz., acetic and formic acids > non-volatile aliphatic acids, viz., citric and oxalic acids > amino acids, viz., glycine and aspatic acid > aromatic acids, viz., *p*-hydroxybenzoic and salicylic acids (Stevenson and Ardakani, 1972; Mench et al., 1988). The concentration of LMWOAs in soils is generally in the range of 10^{-6} to 10^{-3} M (Stevenson, and Ardakani, 1972; Manley and Evans, 1986; Robert and Berthelin, 1986). It has been reported that in soil solution, simple aliphatic acids, amino acids and aromatic acids would be in the range of 1 to 4 x 10^{-3} M, 0.8 to 6 x 10^{-4} M and 0.5 to 3 x 10^{-4} M, respectively (Stevenson and Ardakani, 1972). However, in the soil rhizosphere, the concentration of LMWOAs can be much higher than millimolar due to microbial processes and root exudates (Pareek and Gaur, 1973; Fox and Comeford, 1990). Due to application of sewage sludge to soils, the level of organic acids would be expected to be higher than a millimolar (Hue, 1988). The levels of selected organic acids found in soils is presented in Table 2.4.1.

A wide variety of LMWOAs have been identified in the soil environment (Stevenson, 1967, Stevenson and Fitch, 1986; Huang and Schnitzer, 1986). Low-

molecular-weight organic acids usually comprise only a small fraction of the total mixture of the organic acids in soil solution.

Table 2.4.1 Levels of selected low-molecular-weight organic acids found in soils

Organic acid	Organic acid concentration	References
Acetic (Ethanoic acid)	1 to 5700 μM	Stevenson (1967), Rao & Mikkelson (1977), Hue et al. (1986), Evans & Anderson (1990)
Citric (2-Hydroxy-1, 2, 3-propanetricarboxylic acid)	5 to 14 μM	Bruckert (1970), Hue et al. (1986) Lipton et al. (1987), Evans & Anderson (1990)
Malic (2-Hydroxybutanedioic acid)	3 to 137 μM	Hue et al. (1986), Lipton et al. (1987)
Oxalic (Ethanedioic acid)	4 to 62 μM	Stevenson (1967), Bruckert (1970), Hue et al.(1986), Evans & Anderson (1990)
Succinic (Butanedioic acid)	10 to 282 μM	Hue et al. (1986), Lipton et al. (1987), Hue (1988)

Due to changes in rhizosphere processes, the levels of organic acids in the soil would be expected to change markedly with time. The rhizosphere contains higher quantities of organic acids than nonrhizosphere soil (Stevenson, 1967; Stevenson and Ardakani, 1972). The organic acids isolated, identified and the techniques of identification have been reported in the literature (Stevenson, 1967; Morril et al., 1982; Huang and Schnitzer, 1986; Szmigielska et al., 1995). Oxalic, malic, succinic and citric acids were identified in

the wheat root exudates (Dehay and Carre, 1957; Vancura, 1964). Mench et al. (1988) found that organic acids were major components of the lower-molecular-weight exudates of corn (Zea mays L.). Recently, Szmigielska et al. (1995) reported that the relative abundance of the LMWOAs identified in root exudates of durum wheat cultivars, grown in sterile hydroponic system, followed the order: succinic acid > oxalic acid > malonic acid > fumaric acid.

Cieslinski et al. (1997) reported that the actual amounts of LMWOAs in the root exudates depend upon both the cultivar and the species of the plant. Both aerobic and anaerobic microbial processes were reported to produce acetic acid when rice straw was added to soil as an amendment (Takijima, 1960; Rao and Mikkelsen, 1977). Soil bacteria can synthesize some simple volatile acids, e. g., acetic acid (Stevenson, 1967). Some bacteria are able to produce oxalic acid under acidic conditions (Berthelin and Belgy, 1979). Soil fungi produce mainly non-volatile organic acids, e. g., citric and oxalic acids (Stevenson, 1967). Increased microbial activity is responsible for the most of the organic acids, e.g., succinic and citric acids found in the rhizosphere compared to the bulk soil (Chandrasekaran, 1969).

When nutrient and energy sources are available, microorganisms solubilize heavy metals (e.g., Cd, Pb, and Cu) that were fixed or bound to soil constituents or present in the parent material by production of acid and/or complexing agents (Berthelin et al., 1995). In recent studies by Cieslinski et al. (1996), organic acids were identified in the rhizosphere soil and none in the bulk soil.

Acetic acid and formic acid which are produced by vegetation and ants were reported to be continuously added by dry and wet deposition to scrub-grass savanna and to semideciduous forests of Venezuela (Sanhueza and Andreae, 1991). Bruckert et al. (1971) identified citric, malic, oxalic, succinic, and *p*-hydroxybenzoic acids in washings of plant leaves. Citric, malic and succinic acids were isolated in the root exudates of cereal crops and forage crops (Gardner et al., 1983; Lipton et al., 1987; Hoffland et al., 1989).

Citric and malic acids were produced in higher quantities when plants (alfalfa, rape, lupin) were under P-stress, indicating that release of organic acids may provide mechanism by which P-stressed plants enhance the availability of P in the rhizosphere. The role of LMWOAs in complex formation with metal ions have been reported (Rovira and McDougall, 1967; Rovira, 1969; Stevenson and Fitch, 1986; Robert and Bertelin, 1986). Through the formation of soluble complexes, LMWOAs can modify the mobility of trace metals, e.g., Cd in the soil.

In forest litter extracts, oxalic, acetic, citric, succinic, malic, etc., acids have been isolated (Pohlman and McColl, 1988; Evans and Anderson, 1990; Tam and McColl, 1991). Acetic, citric, malic, oxalic and succinic acids were identified in the root exudates of a variety of vegetables (Vancura and Hovadik,1965) and pine trees (Muir et al, 1964; Smith, 1969, 1976). *p*-Hydroxybenzoic acid was found in the exudates of groundnuts (Reddy and Patrick, 1977). Decomposition of roots and plants produced citric and succinic acids by microbial activities and autolysis (Berthelin, 1982). Malic acid is the predominant acid in unripe apples, grapes, and numerous other fruits and contributes significantly to their flavor (Snell and Ettre, 1969). Oxalic acid has been reported to be one of the most predominant acids in soils (Manley and Evans, 1986; Fox and Comerford, 1990). In the clay loam A horizon of an Alfisol, *p*-hydroxybenzoic acid has been reported (Whitehead et al., 1981).

Organic acids are ubiquitous in soils and exhibit a wide variety of properties. They form surface complexes with soil particles through functional groups like amines, heterocyclic N, carbonyl, carboxylate, amino, alcoholic OH and uncharged nonpolar organic functional groups (Sposito, 1984). Organic acids may be adsorbed by the soil colloids, the degree of which would depend upon the kinds and relative proportions of the soil components. The low-molecular weight organic-acids (LMWOAs), because of their ability to complex trace metals, play a key role in trace metal mobilization and bioavailability in soils.

Mench et al. (1988) reported that metal cations were complexed in the soil rhizosphere by a variety of LMWOAs. Chelation of metals in soil disturbs the equilibrium between the labile metal on the solid phase and soil solution and enhances the release of the former to the solution. Removal of a metal ion by plant uptake thus establishes a diffusion gradient to transport more chelated metal towards the root surface. The stability constants of the Cd-organic acid complexes ($K_{Cd\text{-}LMWOA}$) used in this study are presented in Table 2.4.2.

Table 2.4.2 Stability constants of the Cd-organic acid complexes (log $K_{Cd\text{-}LMWOA}$) (Sillen and Martell, 1964)

Organic acid	Log K
Acetic	1.50
Citric	3.98
Fumaric	N/A†
Malic	2.36
Oxalic	3.89
Succinic	2.10

† Not available

The stability constants of the Cd-organic acid complexes ($K_{Cd\text{-}LMWOA}$) would reflect steric and electrostatic interactions between an organic molecule and Cd in solution. Usually, stable complexes are found to contain 5- and 6-membered rings which involve carboxylic and phenolic groups and a central cation, Cd. The organic acids most effective in forming stable complexes with metal ions are those of the di- and tricarboxylic types (e.g., oxalic and citric, respectively).

2.4.2 Other ionic factors

Soil pH is often regarded as the major variable controlling plant uptake of Cd from soils (Chaney and Hornick, 1978). The role of pH in cadmium distribution and mobility has been reported (Christensen, 1984a). The lower the pH of the system, the more Cd is released from the adsorption sites and consequently increased Cd availability to plants can be expected in acid soils (Peterson and Alloway, 1979). In neutral and acidic soils, precipitation of Cd is unlikely to occur, other than in soils which are calcareous or very high in phosphate or sulfate (Lindsay, 1979). Many studies using a wide range of crops have shown that the increased solubility of Cd at low pH is reflected in an increased Cd uptake by plant (John et al., 1972; McClean, 1976; Reddy and Patrick, 1977).

Other soil and solution factors that influence sorption reactions (e.g., ionic strength, competing effect of other cations, inorganic ligands) will also affect the release of Cd from soils. Chloride may form complexes with Cd (Hahne and Kroontje, 1973), thereby enhancing the release of the dissolved Cd fraction from the soils. The lower sorption of Cd in the presence of Ca will enhance the release of Cd from the soil. This is attributed to the competition for sorption sites between Ca^{2+} and Cd^{2+} ions. Increasing ionic strength has been reported to decrease the amount of Cd sorbed by clays (Garcia-Miragaya and Page, 1976). This should enhance the release of Cd from the soils. These factors which retard Cd adsorption and therefore enhance Cd release from the soil have been discussed in Section 2.3.2 under sorption-desorption of Cd in soils.

Furthermore, the chemical species of Cd in soil solution affects its mobility. The concentration of Cd species in the soil solution of the soil-root interface govern the labile soil Cd. The importance of the metal-organic complex-bound Cd species in determining the availability of Cd in soils was shown by Krishnamurti et al. (1995a). Geisy (1980) reported that the affinity of Cd for organics in the presence of Ca as a competing ion was not greatly affected. Both electronegativity and ionic radius are important parameters in determining the stability of metal-organic complexes (Geisy, 1980). Low affinity for

naturally occurring organics by Ca^{2+} can be explained by its large ionic diameter and low relative electronegativity. For example, Al^{3+} ion with a small ionic radius and relatively high electronegativity has a high affinity for organics. Al is able to successfully compete with Cd for binding sites on organic ligands and often resulted in no organic binding of Cd, resulting in Cd release.

3. EXPERIMENTS, RESULTS AND DISCUSSION

3.1 Status and Speciation of Cadmium in Soils

3.1.1 Background

Because of the increase in agricultural, industrial and urban activities, there has been a great concern over a number of environmental problems arising from the presence of heavy metals, particularly Cd. Cadmium is one of the most toxic and mobile elements found in soils. The potential toxicity of Cd to animals and humans has encouraged research into the presence of this metal in soils, with emphasis on soils treated with sewage sludge or phosphate fertilizers (Rothbaum et al., 1986; De Boo, 1990). On the other hand, the Cd content of natural, unpolluted soils is typically considered as a background content and is given much less attention. Thus, there is a lack of information on the Cd content of most natural soils. The total Cd content of a soil in principle, is related to its content in the original rock on which the soil developed, as well as the alterations undergone by its starting material. The forms in which Cd may be present in different soil horizons and their distribution depend on physical, chemical and mineralogical properties of soils (S'anchez-Camazano, et al., 1994). Trace metals may be distributed among many components of the soil or sediment and may be associated with them in many different ways. The nature of this association has often been referred to as *speciation.* It is the chemical species or forms that determine the mobility and bioavailability of the element. The determination of total content of heavy metals is insufficient to assess the environmental impact of contaminated soils and sediments (Salomons and Forstner, 1980). Determination of various chemical forms of a metal in soils is therefore important to evaluate its mobility and bioavailability.

Single extractants have been used to evaluate the speciation of major elements but it is unlikely that single extractants can give a useful information on metal speciation in soils. Multi-step extraction methods, although more time consuming, provide relatively more detailed information about the status of trace metals in soils (Pickering, 1986). Several sequential extraction methods of soils and sediments have been described in the literature (Gupta and Chen, 1975; Tessier et al., 1979; Shuman, 1979, 1985).

The procedure used extensively for the speciation of particulate-bound heavy metals in soils is that of Tessier et al. (1979), which delineates the metal species sequentially as exchangeable, carbonate-bound, Fe and Mn oxide-bound, organically bound, and residual. Recently Krishnamurti et al. (1995a) developed a selective sequential extraction scheme for partitioning the particulate-bound Cd species as: exchangeable, carbonate-bound, metal-organic complex bound, easily reducible metal-oxide bound, organic-bound, amorphous mineral-colloid bound, crystalline Fe-oxide bound and residual. A number of extractants, which include ammonium acetate-acetic acid-ethylene diamine tetraacetic acid (AAAc-EDTA) (Lakanen and Ervio, 1971) and ammonium hydrogen carbonate-diethylene triamine pentaacetic acid (AB-DTPA) (Soltanpour, 1991), have been used to estimate the plant available trace metals. However, relatively little is known about Cd status and speciation in tropical soils.

The objective of this study was to investigate the speciation of particulate-bound Cd and its importance in influencing the availability index of the soil profiles of selected tropical soils in Kenya.

3.1.2 Materials and Methods

3.1.2.1 Description of the sampling sites

The soil pattern in Kenya is very intricate because of striking differences in altitude, landform (their shape, stability), geology and climate (including past climates) (Sombroek et al., 1982). The soils used in this study were obtained from selected main

agricultural soils in Kenya, varying widely in physicochemical properties. The selected soil sites were Egerton (Andisol, derived from volcanic ash and pyroclastic rocks), Naivasha (Inceptisol, derived from lacustrine deposits, mainly from volcanic ash origin), Kericho (Alfisol, derived from volcanic ash and tertiary igneous rocks), Soy (Oxisol, derived from igneous rocks) and Kitale (Oxisol, derived from metamorphic rocks). The main agricultural areas of Kenya are found within the highland parts of the Rift Valley region (Egerton, Kericho, Kitale and Soy) which receive sufficient annual rainfall to support farming; however, in certain lower parts of the Rift Valley, e.g., Naivasha, vegetables are grown under irrigation. The water used for irrigation in this area is mainly from boreholes. The highland regions of Kenya, namely Kitale and Soy, are the major producers of maize and wheat while in Egerton wheat, barley and maize are grown. Kericho is the major tea producing region in Kenya. The physical conditions of the sampling sites are summarized in Table 3.1.1.

Table 3.1.1 Physical conditions at the sampling sites (Sombroek et al., 1982)

Site	Soil type	Temp. (°C)†	Rainfall (mm)‡	Altitude range (m)
Egerton	Andisol	16.1	1100	2100-2400
Naivasha	Inceptisol	18.0	675	1800-2100
Kericho	Alfisol	16.0	1900	1850-2150
Soy	Oxisol	17.0	1300	2100-2400
Kitale	Oxisol	17.0	1300	1850-2150

† Mean annual temperature

‡ Mean annual rainfall

3.1.2.2 Soil characteristics

The five soils presented in Table 3.1.1 were used in this study. Soil samples were taken from various depths (0-40 cm, 40-70 and 70-100 cm depths) of the fields. In each sampling site, the soil samples were taken from six pits; the distance between the pits was 100 m. The soil samples were then made into one composite sample to represent each sampling site. The soil samples were air dried, and gently ground with a wooden roller to pass through a < 2-mm sieve, homogenized and stored for subsequent analysis. Selected soil properties used in this study are presented in Table 3.1.2. Further details of these properties and other basic properties of the soils studied are presented in the Appendices 6.2 to 6.6.

The pH of the soil samples in water (1:2 soil:water) was measured using a pH meter model 1820P (Fisher Scientific, Pittsburgh, PA). The cation exchange capacity (CEC) of the soils was determined after saturation with ammonium acetate solution according to the method of Jackson (1958). Mechanical analysis of the soils was carried out based on the method outlined by Jackson (1979). The total and organic C content of the soils were determined by heating the soils without any treatment at 1100 °C and 850 °C, respectively using a Leco CR-12 carbon analyzer (Leco Corp. St. Joseph, MI) as recommended by the manufacturers. Inorganic carbon was determined from the difference between the two values. The Fe, Mn, and Al contents of the pyrophosphate extract (McKeague, 1967) and the contents of free Fe and amorphous Fe following the citrate-dithionite-hydrogen carbonate (CDB) extraction method (Mehra and Jackson, 1960), and the ammonium-oxalate-oxalic acid extraction method (McKeague and Day, 1966), respectively, were determined by a Perkin-Elmer 300 atomic absorption spectrometer (Norwalk, CT); the steps and conditions used were the same as those recommended by the manufacturer.

Table 3.1.2 Selected properties of the soils studied

Soil	Parent material	Soil depth	pH	CEC	Mechanical analysis			Org. C	Inorg. C	CDB Fe†	Na -pyrop ‡			Amm. Oxal††		Total Cd
					>50µm	2-50µm	<2µm				Al	Fe	Mn	Al	Fe	
		cm		cmol/kg	%			g kg^{-1}								mg kg^{-1}
Egerton (Andisol)	Volcanic ash	0-40	6.0	14.4	20.6	26.4	53.0	26.0	1.0	35.0	1.4	0.9	0.02	1.7	6.5	0.157
		40-70	5.7	11.7	18.0	26.7	55.3	11.0	0.7	46.0	1.6	0.9	0.03	2.1	11.5	0.089
		70-100	5.8	10.4	23.8	10.8	65.5	2.0	2.1	36.0	1.8	0.5	0.01	1.0	11.5	0.076
Naivasha (Inceptisol)	Lacustrine/ volcanic ash	0-40	6.8	10.2	39.1	11.9	49.0	14.0	2.0	12.0	0.8	0.5	0.10	1.6	0.6	0.119
		40-70	7.8	18.9	30.4	14.6	55.0	10.0	2.7	6.0	0.3	0.2	0.01	1.4	0.5	0.187
		70-100	8.0	18.7	23.8	16.2	60.0	6.0	5.4	4.0	0.1	0.9	0.00	1.2	0.4	0.132
Kericho (Alfisol)	Volcanic ash/igneous rocks	0-40	4.1	13.9	13.2	24.8	62.0	50.0	1.0	54.0	7.4	10.0	0.40	6.7	1.6	0.047
		40-70	4.0	11.8	5.4	25.7	68.9	39.0	0.1	57.0	7.7	9.2	0.20	5.9	1.6	0.041
		70-100	4.0	10.8	2.6	26.4	71.0	20.0	0.4	62.0	3.0	4.5	0.10	5.1	1.9	0.028
Soy (Oxisol)	Igneous rocks	0-40	5.4	9.5	34.7	11.3	54.0	20.0	2.0	17.0	1.3	0.6	0.01	1.9	0.4	0.019
		40-70	5.3	8.6	35.5	7.5	57.0	16.0	1.9	22.0	1.1	0.7	0.01	2.3	1.0	0.006
		70-100	5.6	4.2	72.5	11.5	16.0	5.0	1.4	34.0	0.4	0.2	0.00	0.6	0.8	0.008
Kitale (Oxisol)	Metamorphic rocks	0-40	5.0	7.2	46.7	15.3	38.0	25.0	1.0	29.0	1.2	1.2	0.01	1.7	1.0	0.017
		40-70	5.1	5.5	44.2	11.8	44.0	11.0	1.0	48.0	1.8	0.7	0.03	2.0	1.0	0.007
		70-100	5.0	5.1	41.0	12.0	47.0	10.0	1.0	46.0	0.7	0.7	0.02	2.3	0.7	0.002
$LSD_{0.05}$			0.05	0.08	0.10	0.09	0.96	0.05	0.03	0.5	0.03	0.02	0.01	0.04	0.05	0.001
$LSD_{0.01}$			0.09	0.11	0.14	0.13	1.80	0.07	0.05	1.11	0.07	0.03	0.02	0.06	0.09	0.002

† Citrate-dithionite- hydrogen carbonate extractable Fe

‡ Sodium pyrophosphate extractable Mn, Fe and Al

†† Ammonium oxalate extractable Al and Fe

The minerals present in various particle size fractions were determined by X-ray diffraction (XRD) analysis according to the method of Jackson (1979). In the clay size fraction (< 2 μm), kaolinte was the predominant mineral. The oxides of Al (gibbsite), Fe (goethite, hematite) and Mn (birnessite) were detected in all of the particle size fractions of the soils that were examined using X-ray diffraction analysis (Appendix 6.3). Some of the other minerals that were identified in the various particle size fractions of the soils studied are presented in Appendix 6.3. The point of zero charge (PZC) of the soils was determined according to the method of Duquette and Hendershot (1993) and the specific surface of the soil samples was determined by ethylene glycol monoethyl ether (EGME) method (Eltantawy and Arnold 1973; Tiller and Smith, 1990) and by the BET-N_2 method using Autosorb (Quantachrome Corp., Syosset, N.Y). These properties are in summarized in Table 3.1.3.

3.1.2.3 Total and bioavailable cadmium

For total Cd analysis, the soils were ground with an agate mortar and a pestle to pass through a 140-mesh sieve and homogenized before use. The samples were digested in duplicate following the microwave oven digestion method of Krishnamurti et al. (1994). The digested samples were filtered and washed through Whatman No. 42 filter paper and the filtrates analyzed for Cd using a Perkin Elmer 2180 graphite furnace atomic absorption spectrometer (GFAAS) at 228.8 nm. The determination of total Cd in the filtrate involves the following steps: drying, thermal pretreatment (char), cooling and atomization. Hence, it is necessary to carefully select treatment temperatures and reaction times to ensure that each process is carried out effectively. The furnace parameters which were used to achieve maximum accuracy and sensitivity in the determination of Cd in aqueous extracts are given in Table 3.1.4. Cadmium availability index (CAI) of the soils (< 2 mm) was determined following the AAAc-EDTA extraction procedure (Lakanen and Ervio, 1971).

Table 3.1.3 Point of zero charge and the specific surface of the soils†

Site	PZC	Specific surface ($m^2 g^{-1}$)	
		EGME	BET-N_2
Egerton	6.3	66.3	32.4
Naivasha	7.2	79.0	36.0
Kericho	3.9	109.2	64.8
Soy	5.0	71.1	36.0
Kitale	5.0	44.5	24.6

† Surface soils (0-40 cm depth)

Table 3.1.4 Graphite furnace atomic absorption spectrophotometer parameters used for the determination of Cd (Krishnamurti et al., 1994)

Steps	Temp (^{0}C)	Ramp Time (s)	Hold Time (s)	Argon Flow (ml/min)
Drying	200	10	20	300
Charring	300	5	20	300
Cooling	50	5	15	300
Atomization	1600	0	10	0
Cleaning	2700	5	5	300

3.1.2.4 Sequential chemical extraction of soil cadmium

The particulate-bound Cd species of the soil samples were determined following the eight-step sequential extraction method of Krishnamurti et al. (1995a). The sequential extraction scheme used in this study is summarized in Table 3.1.5. Cadmium in the supernatant was determined using graphite furnace atomic absorption spectrometer as described in Section 3.1.2.3. The chemicals used in the sequential chemical extraction were of analytical grade and de-ionized, distilled water was used in the preparation of their solutions. All glassware used was previously soaked overnight in 10% (v/v) concentrated HNO_3 and rinsed with de-ionized, distilled water just before use.

3.1.3 Results and discussion

3.1.3.1 Total cadmium content

The total Cd content of the surface and subsoils from different geographical regions in Kenya varied with the soil types and generally decreased with soil depth (Table 3.1.2). In the surface soils the total Cd varied between 0.017 and 0.157 mg kg^{-1} (average 0.071 mg kg^{-1}) whereas for the subsoil horizons relatively low values (average 0.058 mg kg^{-1}) were observed with the exception of the Naivasha soil which is derived from lacustrine deposits, mainly of volcanic ash origin. The Naivasha soil was obtained from areas around Lake Naivasha which is situated in the Rift valley part of Kenya. The lake was formed as a result of volcanic activities. It has been reported that Cd is either present quite evenly throughout a given soil profile (Adriano, 1986) or accumulates in the surface horizon, in parallel with humus (Andersson, 1977; Adriano, 1986). A number of factors have been suggested to contribute to Cd accumulation in the surface horizon which is the zone with the highest organic matter content. Metals may be retained in this strongly adsorptive horizon after reaching it as a result of cycling through vegetation, or from applications of Cd-containing fertilizers and manures, or from the wet and dry deposition from the atmosphere (Alloway, 1995). The total Cd content of the soils studied was

Table 3.1.5 Multi-step sequential extraction scheme for particulate-bound Cd speciation used in this study (Krishnamurti et al., 1995a)

Species	Reagent per 1 g of soil	Shaking time and temperature (°C)
Exchangeable	10 mL of 1 M $NaNO_3$	4 h at 25 °C
Carbonate-bound	25 mL of 0.1 M CH_3CO_2Na (pH 5)	6h at 25 °C
Metal-organic complex-bound	30 mL 0.1 M $Na_4P_2O_7.H_2O$ (pH 10)	20 h at 25 °C
Easily reducible metal oxide-bound	20 mL 0.1 M $NH_2OH.HCl$ in 0.1 M HNO_3	30 min at 25 °C
Organic-bound	5 mL, 30% H_2O_2 (pH 2), 3 mL of 0.02 M HNO_3;	2 h at 25 °C
	then add 3 mL 30% H_2O_2 (pH2)	2 h at 25 °C
	cool, add 10 mL 2 M $NaNO_3$ in 20% HNO_3	30 min at 25 °C
Amorphous mineral colloid-bound	10 mL 0.2 M $(NH_4)_2C_2O_4$ (pH 3)	4 h at 25 °C
Crystalline Fe oxide-bound	25 mL 0.2 M $(NH_4)_2C_2O_4$ (pH 3) in 0.1 M ascobic acid	30 min at 95 °C
Residual	Digest residue in the last step by HF-$HClO_4$	

within the range of some tropical soils (e.g., for Tanzania the range is 0.049 to 0.298 mg kg^{-1} soil with an average of 0.123 mg kg^{-1} soil) as reported by Sillanpaa and Jansson (1992).

Table 3.1.6 gives simple correlation coefficients between the content of total soil Cd and soil properties within the soil profiles. Cadmium concentrations were correlated with pH of the soils ($p = 1.2 \times 10^{-3}$). In contrast, there was no correlation between total soil Cd and the contents of clay and organic carbon, or the specific surface of the soils. The Cd content of the soils studied was higher for the soils derived from volcanic ashes (Egerton and Kericho) and lacustrine deposits, mainly of volcanic ash origin (Naivasha) than for the soils derived from igneous rocks (Soy) or metamorphic rocks (Kitale) (Table 3.1.2). The Cd content of the soils is determined by the parent material and its subsequent alterations through weathering processes. According to the geochemistry of Cd, the amounts of Cd in the parent materials would depend upon the composition of the rock (Wakita and Schmitt, 1970). Wakita and Schmitt (1970) and Alloway (1995) reported the range of Cd concentration in various rock compositions, i.e., Igneous rock: rhyolites (0.03-0.57 mg Cd kg^{-1}), granites (0.01-0.1.60 mg Cd kg^{-1}), basalts (0.01-0.60 mg Cd kg^{-1}) ; metamorphic rocks: gneisses (0.007-0.26 mg Cd kg^{-1}) , schists (0.005-0.87 mg Cd kg^{-1}); sedimentary rocks: shales (0.017-11 mg Cd kg^{-1}), black shales (0.30-219 mg Cd kg^{-1}), sandstones and conglomerates (0.019-0.4 mg Cd kg^{-1}), carbonates (0.007-12 mg Cd kg^{-1}), phosphorites (10- 980 mg Cd kg^{-1}) and volcanic ash (4.5 mg Cd kg^{-1}) (Bailey et al., 1995). Many authors have shown that similar starting materials can give rise to soils with varying Cd contents (Tiller, 1989; Alloway, 1995). Page and Bingham (1973) suggested that the soils derived from igneous rocks would have Cd contents of 0.1-0.3 mg kg^{-1}, those on metamorphic rocks would contain 0.1-1.0 mg kg^{-1} and those derived from sedimentary rocks 0.3-11 mg kg^{-1} Cd. The Cd content of soils derived from volcanic ash can be as high as 4.5 mg kg^{-1} (Bailey et al., 1995). In the tropical soils studied, relatively lower values of Cd content were observed. The Cd content of the

surface soils were as follows: Egerton (0.157 mg kg^{-1}), Kericho (0.047 mg kg^{-1}), Naivasha (0.119 mg kg^{-1}), Soy (0.019 mg kg^{-1}) and Kitale (0.017 mg kg^{-1}).

Table 3.1.6 Simple correlation coefficients between total soil Cd and selected soil characteristics in the soil profiles (n = 15)

Soil parameter	r	p
pH	0.752	1.2×10^{-3}
Organic carbon	0.127	6.5×10^{-1}
Clay	0.251	3.7×10^{-1}
Specific surface	0.058	8.5×10^{-1}

3.1.3.2 Cadmium fractionation

The distribution of particulate-bound Cd species of the individual soils determined by sequential chemical extraction is presented in Table 3.1.7. The exchangeable and carbonate-bound Cd were not detectable. The sum of the particulate-bound Cd species (Table 3.1.7) determined by the sequential extraction method of Krishnamurti et al. (1995a) were less than the total Cd content of the soils (Table 3.1.2). Average percent error was 10.6%. The discrepancy is attributed to the analytical error since the residual Cd was determined in the residue (Table 3.1.7) using HF-HClO4 digestion method (Jackson, 1958) and not by subtraction of the sum of the other Cd fractions from the total soil Cd. The average amount of each particulate-bound Cd species in the surface soils followed the order: metal-organic complex-bound (0.026 mg kg^{-1}) > residual (0.021 mg kg^{-1}) > crystalline Fe oxide-bound (0.011 mg kg^{-1}) > organic-bound (0.007 mg kg^{-1}) > amorphous mineral colloid-bound (0.003 mg kg^{-1}) > easily reducible metal oxide-bound (0.001 mg kg^{-1}). In the subsoils, the order was: residual (0.024 mg kg^{-1}) > metal-organic complex-bound (0.014 mg kg^{-1}) > crystalline Fe-oxide-bound (0.006 mg kg^{-1}) >

Table 3.1.7 Distribution of particulate-bound Cd species in the soil profiles

Soil	Depth cm	Cd Species† EX.	CAR	MOC	ERMO	ORG.	AMC	CFeO	RES			Sum††	AAAc-EDTA extractable Cd
		mg kg^{-1}								$LSD_{0.05}$	$LSD_{0.01}$	mg kg^{-1}	
Egerton	0-40	ND‡	ND	0.070	0.002	0.012	0.005	0.014	0.050	0.002	0.003	0.153	0.137
(Andisol)	40-70	ND	ND	0.022	0.005	0.007	0.003	0.012	0.028	0.001	0.002	0.077	0.044
	70-100	ND	ND	0.014	0.004	0.005	0.006	0.020	0.019	0.002	0.004	0.068	0.036
Naivasha	0-40	ND	ND	0.030	0.003	0.014	0.004	0.021	0.045	0.002	0.003	0.117	0.096
(Inceptisol)	40-70	ND	ND	0.038	0.006	0.005	0.018	0.010	0.068	0.001	0.002	0.145	0.064
	70-100	ND	ND	0.031	0.006	0.004	0.012	0.015	0.055	0.002	0.003	0.123	0.057
Kericho	0-40	ND	ND	0.020	0.001	0.003	0.002	0.016	0.003	0.001	0.003	0.045	0.041
(Alfisol)	40-70	ND	ND	0.008	0.002	0.002	0.004	0.004	0.019	0.001	0.002	0.039	0.031
	70-100	ND	ND	0.006	0.002	0.002	0.008	0.002	0.006	0.002	0.003	0.026	0.024
Soy	0-40	ND	ND	0.005	0.001	0.002	0.001	0.003	0.004	0.001	0.002	0.016	0.017
(Oxisol)	40-70	ND	ND	0.001	ND	0.001	ND	0.002	0.001	0.001	0.002	0.005	0.003
	70-100	ND	ND	0.001	ND	ND	ND	0.002	0.003	0.001	0.002	0.006	0.006
Kitale	0-40	ND	ND	0.004	0.001	0.002	0.001	0.003	0.005	0.001	0.002	0.016	0.014
(Oxisol)	40-70	ND	ND	0.001	ND	0.001	ND	0.002	0.002	0.001	0.002	0.006	0.003
	70-100	ND	ND	ND	ND	ND	ND	ND	0.001			0.001	0.001
$LSD_{0.05}$				0.015	0.001	0.002	0.001	0.001	0.010			0.010	0.010
$LSD_{0.01}$				0.020	0.002	0.003	0.002	0.002	0.020			0.019	0.020

† EX: Exchangeable; CAR: carbonate-bound; MOC: metal-organic complex-bound; ERMO: easily reducible metal oxide-bound; ORG: organic-bound; AMC: amorphous mineral colloid-bound; CFeO: crystalline Fe oxide-bound; RES: residual

†† Sum of the particulate-bound Cd species

‡ ND - Not detectable

amorphous mineral colloid-bound (0.005 mg kg^{-1}) > organic-bound (0.003 mg kg^{-1}) > easily reducible metal oxide-bound (0.002 mg kg^{-1}) for the 40-70 cm depth; in the 70-100 cm depth, the order was as follows: residual (0.017 mg kg^{-1}) > metal-organic complex-bound (0.011 mg kg^{-1}) > crystalline Fe-oxide-bound (0.008 mg kg^{-1}) > amorphous mineral colloid-bound (0.005 mg kg^{-1}) > organic-bound = easily reducible metal-oxide-bound (0.002 mg kg^{-1}).

Percent distribution of particulate-bound Cd species in selected soil profiles is presented in Figure 3.1.1. As previously indicated (Table 3.1.7) the five soil profiles, which had different physicochemical properties and were in different geographical zones in Kenya, contained no detectable Cd either in exchangeable or in carbonate-bound forms. Some of the particulate-bound Cd species, namely, metal-organic complex-bound, organic-bound, easily reducible metal oxide-bound, amorphous mineral colloid-bound and crystalline Fe-oxide bound were not detected in some subsoils. Cadmium in the surface soils studied was generally predominantly present in the metal-organic complex-bound form with an average of 37.1% of the total Cd present in the soils; whereas in the subsoils Cd was mainly in the residual form with an average of 43.4% and 37.5% of the total Cd present in the 40-70 cm and 70-100 cm depths, respectively (Figure 3.1.2).

The distribution of Cd in various particulate-bound forms varied with soil types. The Andisol and Inceptisol were the highest in the amounts of all the forms of particulate-bound Cd. The Oxisols contained the lowest amounts of particulate-bound Cd species and the Alfisol was intermediate. The values for the particulate-bound Cd species can be considered as basic information for Cd status of soils (Ramos et al., 1994). The application of the method developed by Krishnamurti et al. (1995a) facilitates delineating the speciation of particulate-bound Cd in the tropical soils, especially the metal-organic complex-bound Cd which was the predominant particulate-bound Cd species in the surface soils.

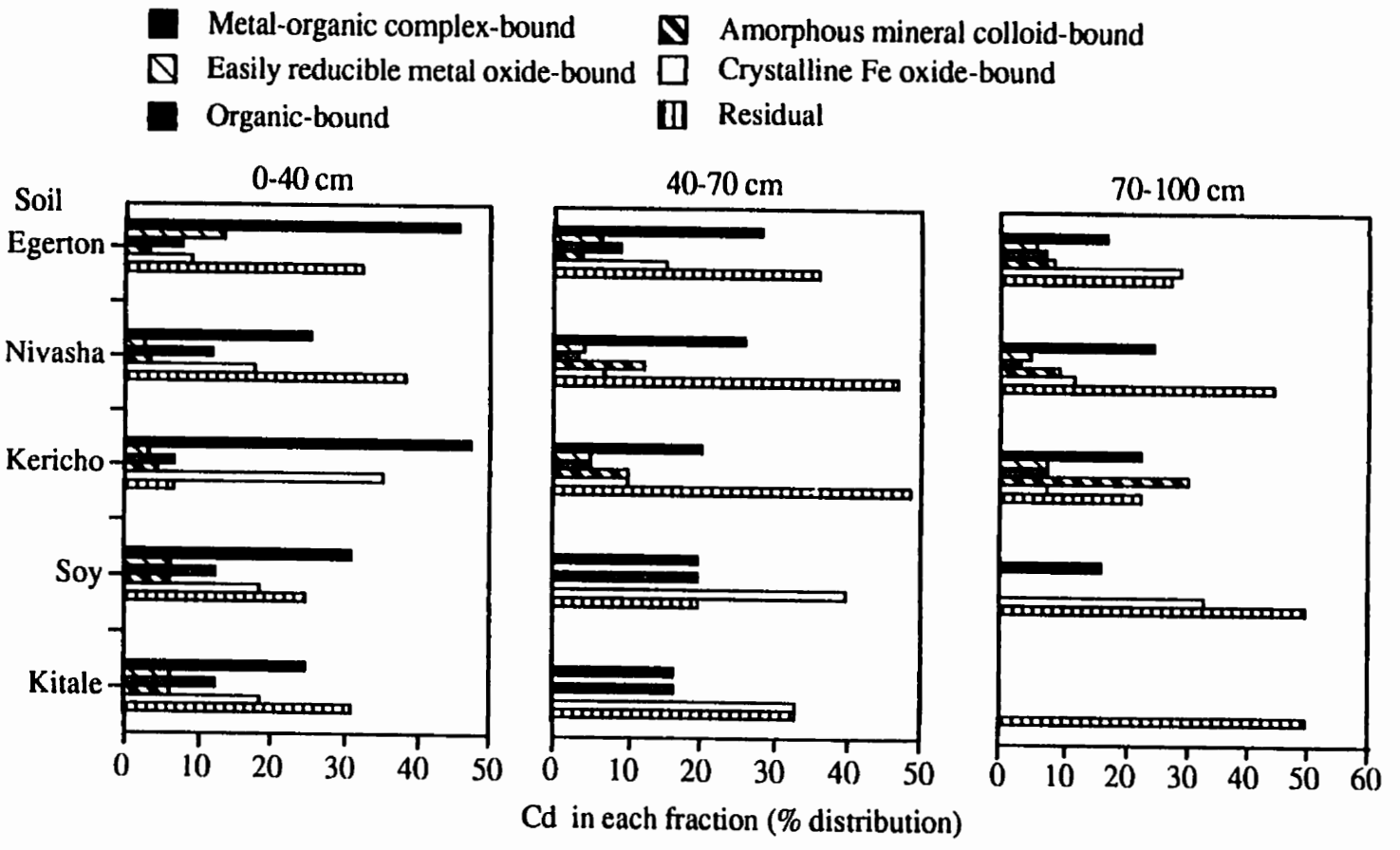

Figure 3.1.1 Percent distribution of particulate-bound Cd species in the soil profiles from Kenya

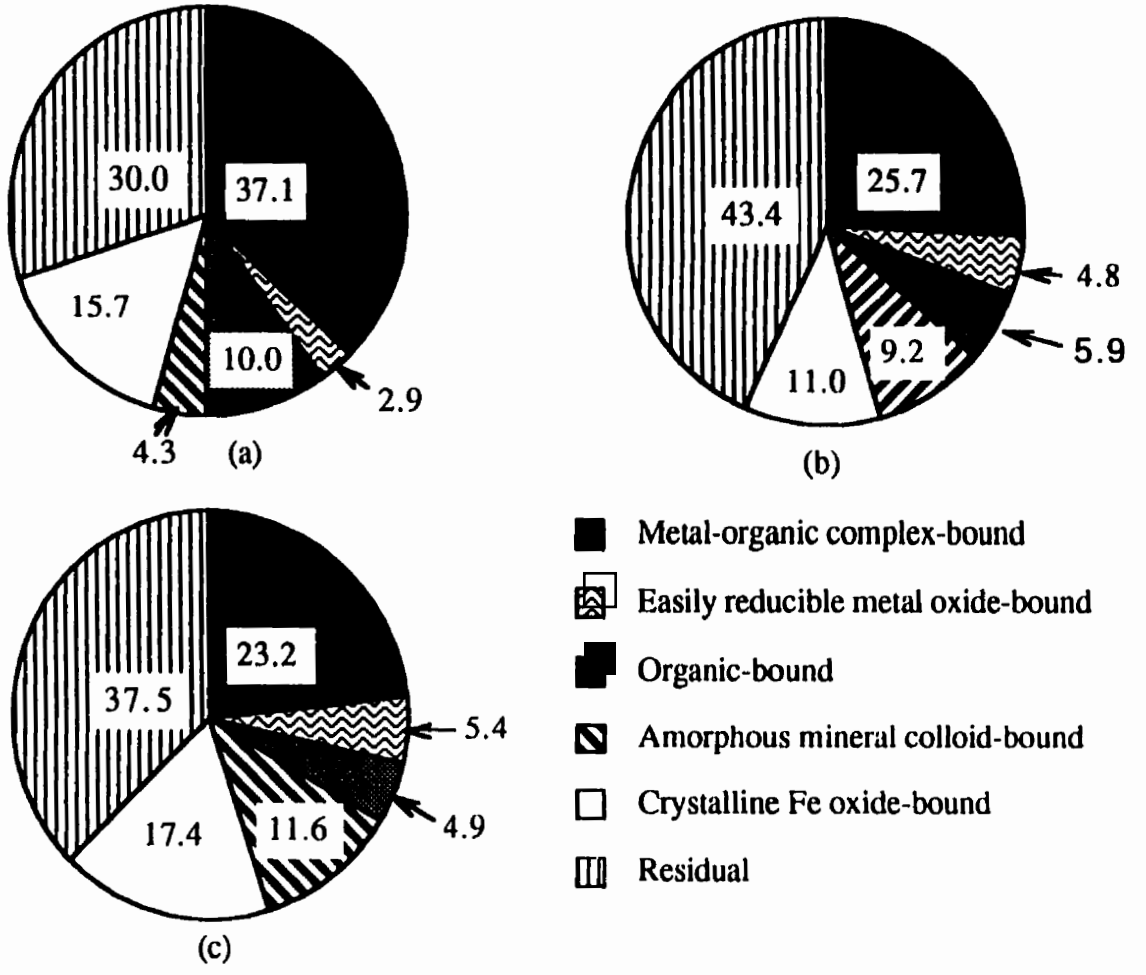

Figure 3.1.2 Average percent distribution of particulate-bound Cd species as a function of soil depth in selected soils from Kenya: (a) 0-40 cm (b) 40-70 cm, and (c) 70-100 cm

3.1.3.3 Particulate-bound cadmium species and cadmium availability index

The AAAc-EDTA extractable Cd has been shown to correlate well with plant Cd and is being used as a reference method for a number of microelements by the European Research Network on Trace Elements; this method has been recommended for acidic soils (Sillanpaa and Jansson, 1992). The available Cd in the selected Kenyan soils which was extracted by the AAAc-EDTA method varied from 0.001 mg kg^{-1} to 0.137 mg kg^{-1} with an average of 0.038 mg kg^{-1} (Table 3.1.7).

In a few cases, it was observed that the Cd availability index (AAAc-EDTA extractable Cd) was much greater than the sum of the metal-organic complex-bound Cd and the organic-bound Cd species. Cd forms strong complexes with EDTA (log $K_{Cd\text{-}EDTA}$ = 16.4) compared to sodium pyrophosphate (log $K_{Cd\text{-}Pyro.}$ = 8.7) (Smith and Martell, 1976). The organic-bound Cd was determined after destruction of organic matter with 30% H_2O_2 using $NaNO_3$ as an extractant (log $K_{Cd\text{-}NO_3^+}$ = 0.5) (Smith and Martell, 1976). The strong chelation between Cd and EDTA, therefore, accounts for the release of more Cd to solution. Also the pH of the AAAc-EDTA extractant was 4.65 whereas the sodium pyrophosphate extraction was carried out at pH 10. At low pH values the solubility of heavy metals is higher, hence more Cd would be present in solution. Furthermore, it has been observed that AAAc-EDTA method tends to give high values compared to other extractants like AB-DTPA, which could be attributed to the solubility of heavy metals at low pH values (pH 4.65) (Krishnamurti et al., 1995a), i.e., the pH at which the extraction was carried out as recommended by Lakanen and Ervio (1971). Nevertheless, tropical soils are often acidic in nature.

The range of AAAc-EDTA extractable Cd of Tanzanian soils was reported to be 0.010-0.040 mg kg^{-1} soil with an average of 0.018 mg Cd kg^{-1} soil for the surface soils (Sillanpaa and Jansson, 1992). The results obtained by Sillanpaa and Jansson (1992) for

the Tanzanian soils showed that the AAAc-EDTA extractable Cd is correlated highly significantly with the Cd content of the plant (maize and wheat).

Simple correlation analysis of the data was carried out to investigate the relationship of the Cd species with the Cd availability index (CAI) in the soil profiles following the standard methods of statistical analysis (Snedecor and Cochran, 1989). The results from simple correlation analysis (Table 3.1.8) showed that, among the particulate-bound Cd species, the amounts of metal-organic complex-bound Cd was correlated most significantly with CAI ($r = 0.960$, $p = 1.63 \times 10^{-8}$), indicating the importance of metal-organic complex bound-Cd in contributing to the Cd availability of the soils studied. The results from simple correlation analysis also showed that organic-bound Cd species was only next to the metal-organic complex-bound Cd species in correlation with CAI ($r = 0.914$, $p = 1.87 \times 10^{-6}$).

Table 3.1.8 Simple correlation coefficients between Cd availability index and particulate-bound Cd species in the soil profiles (n = 15)

Cd species	r	p
Metal-organic complex-bound	0.960	1.53×10^{-8}
Organic-bound	0.914	1.87×10^{-6}
Easily reducible metal oxide-bound	0.498	5.83×10^{-2}
Amorphous mineral colloid-bound	0.451	9.14×10^{-2}
Crystalline Fe oxide-bound	0.715	2.73×10^{-3}
Residual	0.795	3.94×10^{-4}

Further, collinearity test was carried out between the metal-organic complex-bound Cd and the organic-bound Cd (Table 3.1.9). Collinearity refers to the problem of linear

dependence among the predictor variables in multiple linear regression (Baker, 1997). It has been suggested that if the predictor variables are highly intercorrelated, then it becomes difficult to separate the effects of the variables on the dependent variable (Belsley et al., 1980). Belsley et al. (1980) developed a means for detecting one or more collinear relations among a set of variables appearing in a linear regression model,

$y = a + b_1X_1 + b_2X_2 - - - b_nX_n$

where y is dependent variable, a is a constant, $X_1 - - - X_n$ are independent variables and $b_1 - - - b_n$ are regression coefficients in the linear regression equation.

Belsley et al., (1980) and Baker (1997) suggested diagnostic parameters for testing collinearity, i.e., condition index (C1) of the X variable which must be less than 30 and the variance inflation factor (VIF) which must be less than 10 if there is no collinearity between the variables. According to Belsley et al. (1980) a VIF of 10 or more indicate severe collinearity whereas CI of 30 to 100 indicate moderate to strong collinearity and CI of more than 100 indicate severe collinearity.

Table 3.1.9 Collinearity test between metal-organic complex-bound Cd and organic-bound Cd species of the soil profiles

Cd species	Variance inflation factor	Condition index
Metal organic complex-bound	2.33	2.89
Organic-bound	2.33	4.89

The results from the collinearity test using a Statistical Analysis System program (SAS Inst. Inc., 1989) showed that the values for the variance inflation factor (VIF) were

less than 10 whereas the values for the condition index were less than 30. Therefore, there was no collinearity between the metal-organic complex bound-Cd and the organic bound-Cd of the soils (Table 3.1.9). The information is in accord with the fact that the metal organic-complex-bound Cd species and the organic bound-Cd species are not from the same binding site. In the case of the metal-organic complex-bound Cd, the Cd is bound to the reaction sites of the complexes. In contrast, the Cd is bound to the reaction sites of organic matter in the case of the organic-bound Cd.

3.1.4 Summary and conclusions

Both total Cd and the Cd availability index (CAI) which was taken as AAAc-EDTA extractable Cd generally decreased from the topsoil to the subsoil and varied with the soil type. The total Cd content of the soils derived from volcanic ash or lacustrine deposits of volcanic ash origin were higher compared to the soils derived from igneous rocks or metamorphic rocks. The data on the chemical speciation of particulate-bound Cd obtained using the sequential extraction scheme of Krishnamurti et al. (1995a) on selected tropical soils from main agricultural areas in Kenya showed that Cd was neither present in exchangeable nor in carbonate-bound forms. Cadmium in the surface soils was present mainly in the metal-organic complex-bound form which accounted for 25.0 to 45.8% with an average of 37.1% of the total Cd present in the soils. In the subsoils, Cd was present mainly in the residual form which accounted for 20.0 to 48.7% with an average of 43.4% in the 40-70 cm depth and 23.1 to 50.0% with an average of 37.5% in the 70-100 cm depth of the total soil Cd present in the soils. The distribution of Cd in the various chemical forms generally varied with the soil types.

Statistical analysis of the data for the soil profiles showed that AAAc-EDTA-extractable Cd (CAI) most significantly correlated with the amount of Cd bound with the metal-organic complexes ($r = 0.960$, $p = 1.53 \times 10^{-8}$), indicating the importance of metal-organic complex-bound Cd in contributing to the Cd availability in the soils studied. The

organic-bound Cd was next to the metal-organic complex-bound Cd species in correlation with CAI ($r = 0.914$, $p = 1.87 \times 10^{-6}$). Collinearity test showed that there was no collinearity between metal-organic complex bound-Cd and the organic-bound Cd, indicating that the metal-organic complex bound Cd and the organic-bound Cd are not from the same binding site. The statistical results are in accord with the fact that different chemistries are involved in the formation of the metal-organic complex-bound and the organic-bound Cd. In the case of the metal-organic complex-bound Cd, the Cd is bound to the reactive sites of the complexes, whereas in the organic-bound Cd, the Cd is bound to the reactive sites of the organic matter. The information obtained from the study of Cd content and speciation in the soils is fundamental for establishing a soil Cd database and is of significance in interpreting the importance of Cd speciation in Cd bioavailability in tropical soils.

3.2 Fate of Cadmium Introduced to the Soils

3.2.1 Background

The fate of heavy metals, e.g., Cd added to soils including their subsequent distribution in different forms or species and availability is of critical importance in relation to human health. The application of phosphate fertilizers to overcome phosphorus deficiencies in tropical soils may lead to Cd accumulation in these soils since Cd is present in phosphate fertilizers as a contaminant. Phosphate fertilizers are among the several sources of Cd in agricultural soils and their use is so widespread that they present a non-negligible source of Cd pollution (Schroeder and Balassa, 1963; Williams and David, 1976; Reuss et al., 1978). Moreover, phosphates appear to be one of the controlling factors in Cd movement in soils (Wagann et al., 1978). Therefore,
the interaction among phosphates and Cd is of great interest. Williams and David (1973) reported that application of phosphatic fertilizers to some Australian soils resulted in the accumulation of Cd in these soils. The extent of build up of Cd varies with the soil type,

Cd content in the fertilizers and the management practices used (Mortvedt et al., 1981; Tiller et al., 1984; Rothbaum et al., 1986; Barrow, 1987; Alloway, 1995; Mann and Ritchie, 1993). The slow soil processes over several years may change the forms, extractability and bioavailability of the metals (Bell et al., 1991). Regardless of how Cd enters soil systems, the chemical and biological factors of the soil eventually control its uptake by plants and its mobility in soils (Jones and Jarvis, 1981). Chemical form of Cd added to soil has been reported as one of the factors that affect its solubility, mobility and bioavailability in the soil (Street et al., 1978). Changes in the forms of Cd with time could affect its uptake by plants and hence the Cd accumulation in the food chain. In studies conducted by Sidle and Kardos (1977) and King (1988), it was shown that Cd adsorbs onto soil surfaces very quickly. In other studies, it has been reported that adsorption continues for longer periods of time (Brummer et al., 1988). However, Christensen (1984a) observed that more than 95% of the Cd sorption takes place within 10 min, equilibrium being reached in 1 h, and exposures up to 67 weeks did not reveal any long term changes in Cd sorption capacities.

The retention of Cd or any other metals by soils appears to be a multistep process involving an initial fast adsorption (from soil solution to the external soil surface) followed by slow adsorption, i.e., diffusion into inner soil surfaces (Kinniburgh and Jackson, 1981; Brummer et al., 1988; Aringhieri et al. 1985). The changes in Cd to various chemical forms in the soil solution may have important implication in determining its bioavailability. Several studies have shown that Cd in P-fertilizers is available to plants (Schroeder and Balassa, 1963; Williams and David, 1973; Mulla et al., 1980; Mortvedt and Giordano, 1977). Factors reported to affect the plant uptake and solubility and mobility of Cd in the soil include soil pH, chemical form of Cd added, soil cation exchange capacity, soil redox potential, texture, organic matter content, and plant species (John et al., 1972; Haghiri, 1974; Andersson and Nilsson, 1974; Iwai et al., 1975). Cadmium in soil changes into less available forms with time, and this could affect its

uptake by plants (Brams and Anthony 1988; Bell et al., 1991). There is some evidence that Cd availability to plants decreases with time (Street et al., 1978).

The effect of time on the forms of native and added Cd was studied in some West Australian soils (Mann and Ritchie, 1994). Sequential extraction which was carried out at different time intervals after the addition of Cd showed that Cd added to the soils transformed with time to less soluble and less extractable forms, the extent of transformation depending on the type of soil. However, information on the effects of residence time on the transformation of particulate-bound Cd species in soil is so far lacking. The fate of Cd introduced to soils, including its reactions and mobility in the soil and its subsequent uptake and distribution in plants, is therefore of critical importance in relation to human health.

The objective of this study was to investigate the effect of residence time on the transformation of Cd introduced to the soils to various particulate-bound Cd species and its impact on Cd availability index.

3.2.2 Materials and Methods

3.2.2.1 Incubation procedures

Three surface soils, Egerton (Andisol), Naivasha (Inceptisol) and Soy (Oxisol) derived from different parent materials (Table 3.1.2) were selected in this study. The Egerton soil is derived from volcanic ashes and other pyroclastic rocks. The soils in this area are well drained, very deep, dark reddish brown with humic topsoil. The Naivasha soil is derived from lacustrine deposits, mainly of volcanic ash origin. The soils are imperfectly drained, moderately deep to deep. The soils are found in the lake region (lake Naivasha) of central Rift valley. The Soy soil is derived from intermediate igneous rocks (syenites, trachytes and phonolites). The soils are well drained, moderately deep to deep, dark red, friable clay over petroplinthite. The general properties of these soils were presented in Table 3.1.2.

The soil samples were air dried and crushed to pass through a 2-mm sieve. To each 100 g of soil sample, the Idaho monoammonium phosphate (MAP)-fertilizer or the Cd perchlorate-added monoammonium phosphate (MAP) chemical reagent was added to give a Cd content of 62.4 mg kg^{-1} soil. The MAP chemical reagent was very low in Cd content (0.005 mg Cd kg^{-1}). A sample calculation for the amount of Cd added to the soil is shown in Appendix 6.1. Perchlorate was chosen because it forms the least stable complex with Cd, however it may cause some side effects by oxidizing the organic matter. The amount of Cd perchlorate added was 0.0231 g and it is, thus, unlikely that this amount is enough to oxidize a significant portion of the organic matter during incubation. The amount of Cd added to the soils was calculated based on the fertilizer recommendation for these soils (130 kg monoammonium phosphate fertilizer /ha or 67.6 kg P_2O_5 /ha; fertilizer type, 11:52:0) (Annual Farmers' Recommendations, 1993) , the Cd content of the fertilizer, and the amount of soil that would be in contact with fertilizer granules (Appendix 6.1). The soils were placed in plastic containers in two replicates and wetted to field capacity and allowed to incubate at room temperature (25°C) for 15, 50 and 100 days. The plastic containers were covered with parafilm to reduce evaporation. During the incubation period the moisture was kept to field capacity. Control soils were also kept at the same moisture conditions. At the end of each incubation period, sufficient soil was removed from each treatment, air dried and used in the subsequent analyses.

3.2.2.2 Speciation of particulate-bound cadmium of the soils

At the end of each incubation period, particulate-bound Cd species of the Egerton and Naivasha soils were investigated using the sequential extraction method of Krishnamurti et al. (1995a). The sequence of the extraction procedure was presented in Table 3.1.5. Sequential extraction for the determination of particulate-bound Cd species was carried out in duplicate on 1.0 g of control soils or the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent treated soils in 50 mL polypropylene centrifuge

tubes to allow centrifuge washing of the soil after each extraction, thus minimizing any loss of the solids. After each successive extraction, the supernatant liquid was removed by centrifugation for 10 min at 12,000 *g*. The residue was washed with 5.0 mL of deionized distilled water by centrifugation for 10 min at 12,000 *g* and the supernatant liquids were combined, mixed and made up to a volume for the determination of Cd species. Cadmium in the supernatant liquid was determined by graphite furnace atomic absorption spectrophotometer (GFAAS) at wavelength 228.8 nm. The furnace parameters were the same as reported earlier in Table 3.1.4.

3.2.2.3 Cadmium availability index of the soils

The 1 M NH_4Cl method (Krishnamurti et al., 1995b) was used to investigate the effect of incubation time on Cd availability. The M NH_4Cl extractable Cd was used as the Cd availability index in this study because the stability constants of Cd-chloride complexes (log $K_{CdCl^+} = 1.98$; log $K_{CdCl_2^0} = 2.50$; log $K_{CdCl_3^-} = 2.60$; log $KCdCl_4^{2-} = 2.80$) (Smith and Martell, 1976; Dean , 1992) are of the similar order of magnitude as those of Cd-organic acid complexes of many low-molecular-weight-organic acids present in the soil rhizosphere (Krishnamurti et al., 1995b).

Five grams of control soil, the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent treated soil in duplicate was weighed into a 50-mL polypropylene centrifuge tube and 30 mL of 1 M NH_4Cl solution was added. The soil suspension was shaken on a horizontal shaker for 16 h at 25°C at 180 cycles per min. The suspension was then centrifuged at 2,500 g for 5 min and the supernatant liquid was filtered through 0.45 μm filter membrane under vacuum. Cadmium in the supernatant liquid was analyzed using pyrolytically coated graphite tubes fitted with a L'vov platform in a Perkin Elmer HGA 400 graphite furnace coupled to a PE 2280 atomic absorption spectrophotometer with background correction at the wavelength of 228.8 nm. The furnace parameters were the same as those reported earlier in Table 3.1.4. In order to eliminate potential matrix

effects of salt in the extracting solution during analysis, Cd standards were prepared in the same extracting salt solution.

3.2.2.4 Determination of cadmium in different size fractions after incubation

At the end of an 100-day incubation period, different size fractions of the control and treated soils were separated after sonification (Krishnamurti and Huang, 1987). Total Cd content was determined in the different size fractions by the HF-$HClO_4$ digestion method of Jackson (1958). The distribution of individual particulate-bound Cd species in the clay size fraction was determined in the treated soils by the method of Krishnamurti et al. (1995a).

3.2.3 Results and discussion

3.2.3.1 Speciation of particulate-bound cadmium of the treated soils

Particulate-bound Cd species were investigated on two soils (Egerton and Naivasha) at the end of each incubation time. The Cd added was transformed to a series of particulate-bound Cd species (Tables 3.2.1 and 3.2.2). Changes in individual particulate-bound Cd species with time in the treated soils (Idaho MAP-fertilizer or Cd perchlorate-added MAP chemical reagent) showed that except for the residual Cd which steadily increased with the incubation time, the rest of the particulate-bound Cd species significantly decreased with increasing incubation time (Figure 3.2.1 and Appendix 6.9). The results shown are for the Egerton soil since the Naivasha soil also followed the same trend. In section 3.1.3.3, it was observed in the natural soils (Table 3.1.8) that the residual Cd was significantly related to Cd availability ($r = 0.795$, $p = 3.94 \times 10^{-4}$); however, the level of significance of the correlation of the organic-bound Cd ($r = 0.914$, $p = 1.87 \times 10^{-6}$) and the metal-organic complex-bound Cd ($r = 0.960$, $p = 1.53 \times 10^{-8}$) with the Cd availability index were two and four orders of magnitude, respectively, higher compared with the residual Cd. The increase in residual Cd during incubation with time,

Table 3.2.1 Transformation of particulate-bound Cd species in the Egerton soil treated with the Idaho MAP-fertilizer or the Cd perchlorate-added monoammonium phosphate chemical reagent during incubation period

Incubation period (days)	Treatment	Cd introduced to soil (mg/kg)	Particulate-bound Cd species†									
			Exch.	Carb.	MOC	Org.	ERMO	AMC	CFeO	Resid.		
			mg of Cd kg^{-1} soil								$LSD_{0.05}$	$LSD_{0.01}$
	Control§	0	Nd††	Nd	0.070	0.012	0.002	0.005	0.014	0.050	0.001	0.003
15	Idaho MAP‡	62.4	0.57	0.23	30.89	18.04	2.89	1.96	4.21	3.62	0.07	0.11
	MAP + Cd‡‡	62.4	0.68	Nd	34.84	14.46	3.98	0.96	4.78	2.68	0.21	0.32
50	Idaho MAP	62.4	0.50	0.21	28.60	16.02	2.58	1.85	4.00	8.65	0.10	0.26
	MAP + Cd	62.4	0.40	Nd	33.82	14.27	3.98	0.83	4.65	4.45	0.06	0.10
100	Idaho MAP	62.4	0.31	0.12	22.57	14.66	1.88	0.99	3.85	18.02	0.05	0.08
	MAP + Cd	62.4	0.25	Nd	31.15	12.51	3.56	0.76	4.39	9.77	0.06	0.09
$LSD^{¶}_{0.05}$			0.01	0.01	0.07	0.06	0.04	0.05	0.04	0.05		
$LSD^{¶}_{0.01}$			0.03	0.02	0.10	0.11	0.07	0.08	0.07	0.08		

† Exch.: exchangeable; Carb.: carbonate-bound; MOC: metal-organic complex-bound; Org.: organic-bound; ERMO: easily reducible metal oxide-bound; AMC: amorphous mineral colloid-bound; CFeO: crystalline Fe oxide-bound, and Resid.: residual

§ Control soil treated only with the deionized distilled water

†† Not detectable

‡ Idaho monoammonium phosphate-fertilizer

‡‡ Monoammonium phosphate chemical reagent + $Cd(ClO_4)_2$ (Cd content of MAP chemical reagent = 0.005 mg kg^{-1})

¶ LSD for the Cd species in the treated soils

Table 3.2.2 Transformation of particulate-bound Cd species in the Naivasha soil treated with the Idaho MAP-fertilizer or the Cd perchlorate-added monoammonium phosphate chemical reagent during incubation period

Incubation period (days)	Treatment		Particulate-bound Cd species†									
			Exch.	Carb.	MOC	Org.	ERMO	AMC	CFeO	Resid.		
		Cd introduced to soil (mg/kg)	mg of Cd kg^{-1} soil								$LSD_{0.05}$	$LSD_{0.01}$
	Control§	0	Nd††	Nd	0.030	0.014	0.003	0.004	0.021	0.04	0.001	0.003
15	Idaho MAP‡	62.4	0.53	1.54	24.51	16.86	6.02	2.80	4.81	5.31	0.05	0.07
	MAP + Cd‡‡	62.4	0.44	Nd	33.28	14.39	5.25	3.22	4.34	1.49	0.04	0.07
50	Idaho MAP	62.4	0.46	1.28	24.10	14.61	5.34	2.19	4.01	10.41	0.05	0.07
	MAP+ Cd	62.4	0.38	Nd	33.02	14.06	5.00	2.75	4.22	10.41	0.33	0.50
100	Idaho MAP	62.4	0.21	1.15	21.90	13.75	3.46	1.30	3.98	16.63	0.04	0.07
	MAP + Cd	62.4	0.29	Nd	28.56	12.32	4.97	2.15	4.07	10.02	0.21	0.47
$LSD^{¶}_{0.05}$			0.01	0.03	0.44	0.69	0.04	0.05	0.06	0.17		
$LSD^{¶}_{0.01}$			0.04	0.05	0.66	1.05	0.09	0.08	0.09	0.27		

† Exch.: exchangeable; Carb.: carbonate-bound; MOC: metal-organic complex-bound; Org.: organic-bound; ERMO: easily reducible metal oxide-bound; AMC: amorphous mineral colloid-bound; CFeO: crystalline Fe oxide-bound, and Resid.: residual

§ Control soil treated with deionzed distilled water only

†† Nd- Not dectectable

‡ Idaho monoammonium phosphate-fertilizer

‡‡ Monoammonium phosphate chemical reagent + $Cd(ClO_4)_2$ (Cd content of MAP chemical reagent = 0.005 mg kg^{-1})

¶LSD values for the Cd species in the treated soils

therefore, indicates that the Cd added was transformed into less available forms. The formation of reaction products in soil during incubation was apparently responsible for fixation of soil Cd with time. The metal-organic complex bound-Cd and the organic bound-Cd seemed to drop more rapidly in the case of the Idaho MAP-fertilizer treated soil (Figure 3.2.1) and this could account for the sharp increase in the residual Cd (Figure 3.2.1) for the Idaho MAP-fertilizer treated soil. The Cd present as impurities in the Idaho MAP-fertilizer was apparently fixed by the soil.

Speciation studies also revealed that metal-organic complex-bound Cd was the most predominant Cd species and on average accounted for 34.4% of the total Cd in the control soils, 35.6% in the soils treated with the Idaho MAP-fertilizer and 47.8% in the soils treated with the Cd perchlorate-added MAP chemical reagent (Figure 3.2.2).

3.2.3.2 Effect of incubation time on cadmium availability index of the soils

The M NH_4Cl extractable Cd (Krishnamurti et al, 1995b) of the control soils and the soils treated with the Idaho MAP fertilizer or the Cd perchlorate-added MAP chemical, as a function of incubation time, was investigated. The amounts of Cd extracted by M NH_4Cl from the soils treated with the Idaho MAP fertilizer or the Cd perchlorate-added MAP chemical reagent decreased significantly with increasing incubation time (Table 3.2.3 and Appendix 6.10). The increase in residual Cd with time (Figure 3.2.1) indicates that the Cd added was transformed into less available forms which accounts for the decrease in M NH_4Cl extractable Cd with time.

The M NH_4Cl extracted relatively more Cd from the Cd perchlorate-added MAP chemical reagent treated soils than from the Idaho MAP-fertilizer treated soils. In Figure 3.2.1, it was indicated that metal-organic complex bound-Cd and organic bound-Cd appeared to drop more rapidly in the soils treated with Idaho MAP-fertilizer than in the soils treated with the Cd perchlorate-added MAP chemical reagent. At the same time,

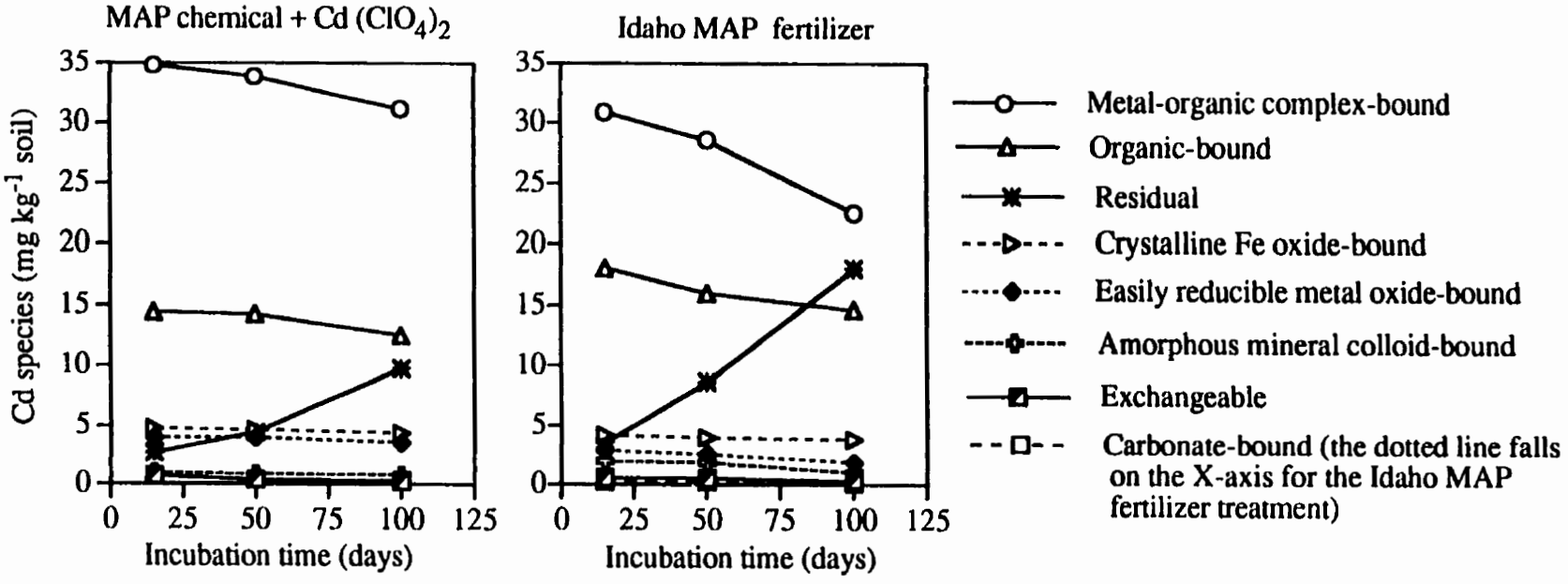

Figure 3.2.1 Relationship between incubation time and particulate-bound Cd species of the Egerton soils treated with the Idaho monoammonium phosphate (MAP)-fertilizer or the cadmium perchlorate-added MAP chemical reagent

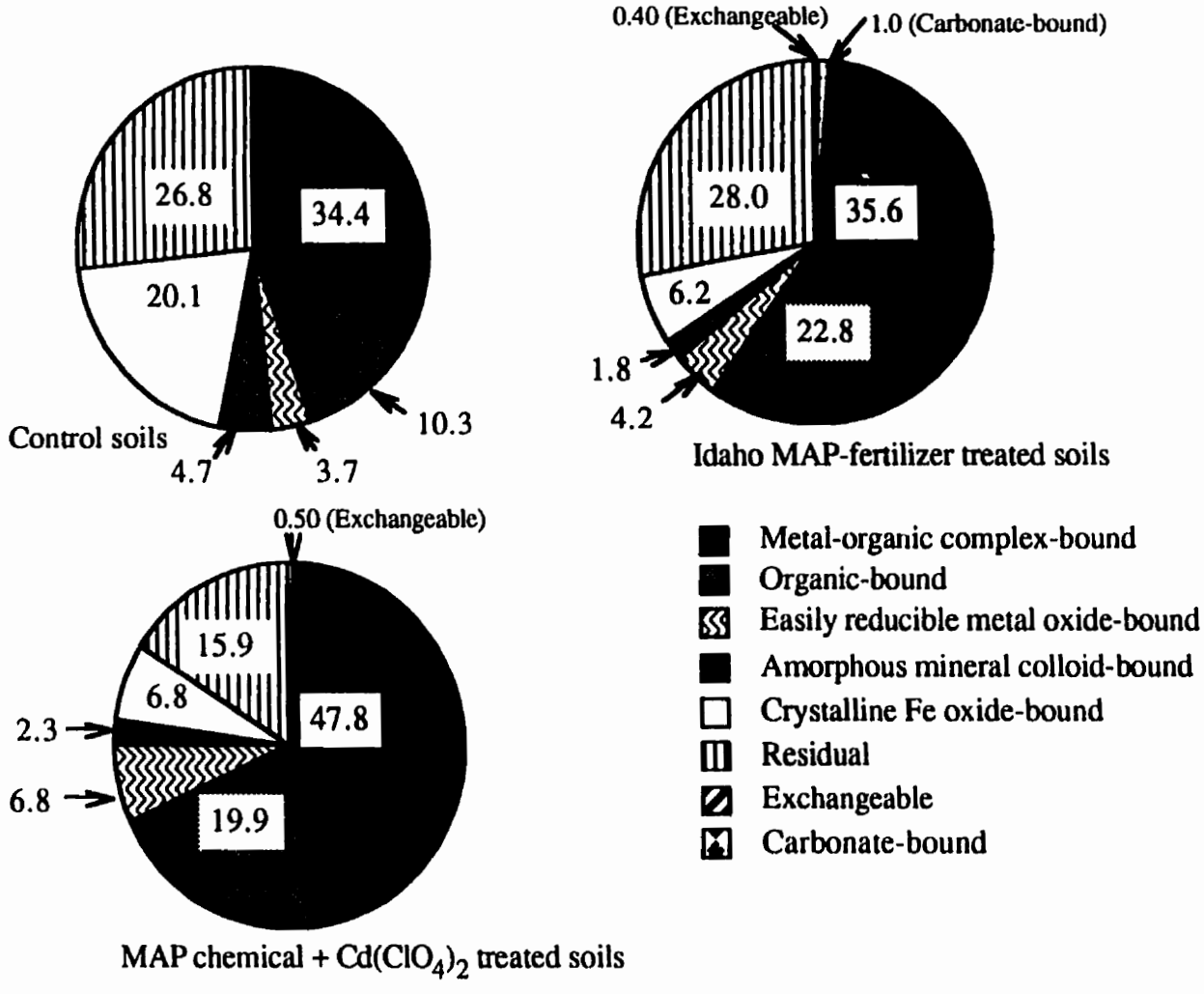

Figure 3.2.2 Average percent distribution of particulate-bound Cd species in the control soils and the soils treated with the Idaho monoammonium (MAP)-fertilizer or the cadmium perchlorate-added MAP chemical reagent after an 100-day incubation period

Table 3.2.3 Residence time effects on the M ammonium chloride extractable Cd of the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added monoammonium phosphate chemical reagent

	Soils										
	Egerton			Naivasha			Soy				
	Reaction time (d)			Reaction time (d)			Reaction time (d)				
Soil treatment	15	50	100	15	50	100	15	50	100	$LSD_{0.05}$	$LSD_{0.01}$
	Extractable Cd (mg kg^{-1} soil)†										
Control‡	0.10	0.10	0.10	0.06	0.06	0.05	0.01	0.01	0.01	0.01	0.02
Idaho MAP-fertilizer‡‡	1.45	1.28	1.13	1.30	1.20	1.04	1.37	1.26	1.11	0.04	0.06
MAP + $Cd(ClO_4)_2$‡‡	8.93	6.56	3.28	5.07	4.70	2.22	8.70	6.24	2.41	0.15	0.30
$LSD¶_{0.05}$	0.09	0.09	0.08	0.09	0.11	0.10	0.09	0.07	0.05		
$LSD¶_{0.01}$	0.22	0.21	0.18	0.21	0.24	0.28	0.22	0.15	0.09		

† NH_4Cl-extractable Cd

‡ The soils were incubated with deionized distilled water

‡‡ Amount of Cd introduced to each soil: 64.2 mg kg^{-1} soil

¶ LSD values for the amounts of NH_4Cl extractable Cd in the treated soils

there was a sharp increase in the residual Cd in the case of the soils treated with the Idaho MAP-fertilizer (Figure 3.2.1). This could explain why the M NH_4Cl extracted more Cd from the Cd perchlorate-added MAP chemical reagent treated soils than from the Idaho MAP-fertilizer treated soils. It was also observed that the amounts of Cd extracted by M NH_4Cl from the soils treated with the Cd perchlorate MAP chemical reagent decreased with time more rapidly compared to the Cd present as an impurity in the phosphate fertilizer (Figure 3.2.3). Apparently, Cd present in the phosphate fertilizer was transformed to residual form with time (residual Cd rapidly increased with time) (Figure 3.2.1). Further, the difference in the NH_4Cl extractable Cd between the soils treated with the Idaho MAP fertilizer and the Cd perchlorate-added MAP chemical reagent is possibly due to the formation of insoluble reaction products between the Cd present in the phosphate fertilizer and the soils since it was observed that over 97% of the Cd was extracted by M NH_4Cl from the Idaho MAP-fertilizer in the absence of soil. The Cd present in the Idaho MAP-fertilizer was apparently in different forms. The reactions of these Cd forms with soils resulted in the differences observed between the NH_4Cl extractable Cd from the Idaho MAP-fertilizer treated soils and the Cd perchlorate-added MAP chemical reagent treated soils.

The M NH_4Cl extractable-Cd was taken as cadmium availability index (CAI) of the soils (Krishnamurti et al., 1995b). The results show that the availability index of Cd in the treated soils varied with the form of Cd introduced to soil and soil type, and also decreased with time (Figure 3.2.3). For comparison, the AAAc-EDTA extraction (Lakanen and Ervio, 1971) was also performed on the Egerton and Naivasha soils at the end of an 100-day incubation period. The individual amounts of the AAAc-EDTA extractable Cd and the NH_4Cl extractable Cd for the Egerton and Naivasha soils are presented in Table 3.2.4. It was observed that the AAAc-EDTA extractable Cd values were higher than the NH_4Cl extractable Cd values for the control soils and the treated soils (Table 3.2.4), which could be partially attributed to the ability of EDTA to form

stronger complexes with Cd (log $K_{Cd\text{-}EDTA}$ = 16.4) compared with Cd-chloride complexes (log K_{CdCl^+} = 1.98, log $K_{CdCl_2^0}$ = 2.50, log $K_{CdCl_3^-}$ = 2.60, log $K_{CdCl_4^{2-}}$ = 2.80) (Smith and Martell, 1976; Dean, 1992). The pH values of the AAAc-EDTA extractant (4.65) and 1 M NH_4Cl solution (pH = 4.14) were of the same order of magnitude hence pH was not a major factor in contributing to the differences in the amounts of Cd extracted by AAAc-EDTA or M NH_4Cl solutions. The EDTA has a strong chelating ability compared to M NH_4Cl and, therefore, has been used to solubilize poorly crystalline Fe oxides and their associated trace metals (Borggaard, 1979).

In the control soils, extractable Cd did not change with time. In the case of treated soils, the decrease in the extractable Cd with time (Figure 3.2.3) indicates that Cd was increasingly transformed to residual Cd (Figure 3.2.1). Transformation of Cd into less available forms with time was also indicated in the studies conducted by Mann and Ritchie (1994). Using sequential extraction, Mann and Ritchie (1994) observed that increase in the time of contact of Cd decreased soluble and exchangeable forms of Cd in the soils. However, they did not use any of the extractants to investigate Cd availability index of the soils hence they did not show any changes in Cd availability index of the soils with the incubation time. Further, Mann and Ritchie (1994) did not investigate the changes in metal-organic complex-bound Cd of the soils with the residence time.

Increasing incubation time could reduce plant availability of the inorganic Cd by one of the following mechanisms: (i) reversion of weakly adsorbed Cd on soil components (clays, metal oxides, organic matter) to stronger and stable forms, (ii) transformation of freshly precipitated Cd to more ordered and less soluble forms, and/or (iii) immobilization of Cd by microbial action. The formation of $Cd_3(PO_4)_2$ (K_{sp} = 2.5 x 10^{-33}, Dean, 1992) in soil solution and/or the adsorption of Cd by soil particles could result in the decrease of Cd availability with time, leading to Cd accumulation in soils. Takijima and Katsumi (1973) found that P may restrict Cd movement in soils probably because of the formation of sparingly soluble salts with Cd in soil. Organic matter,

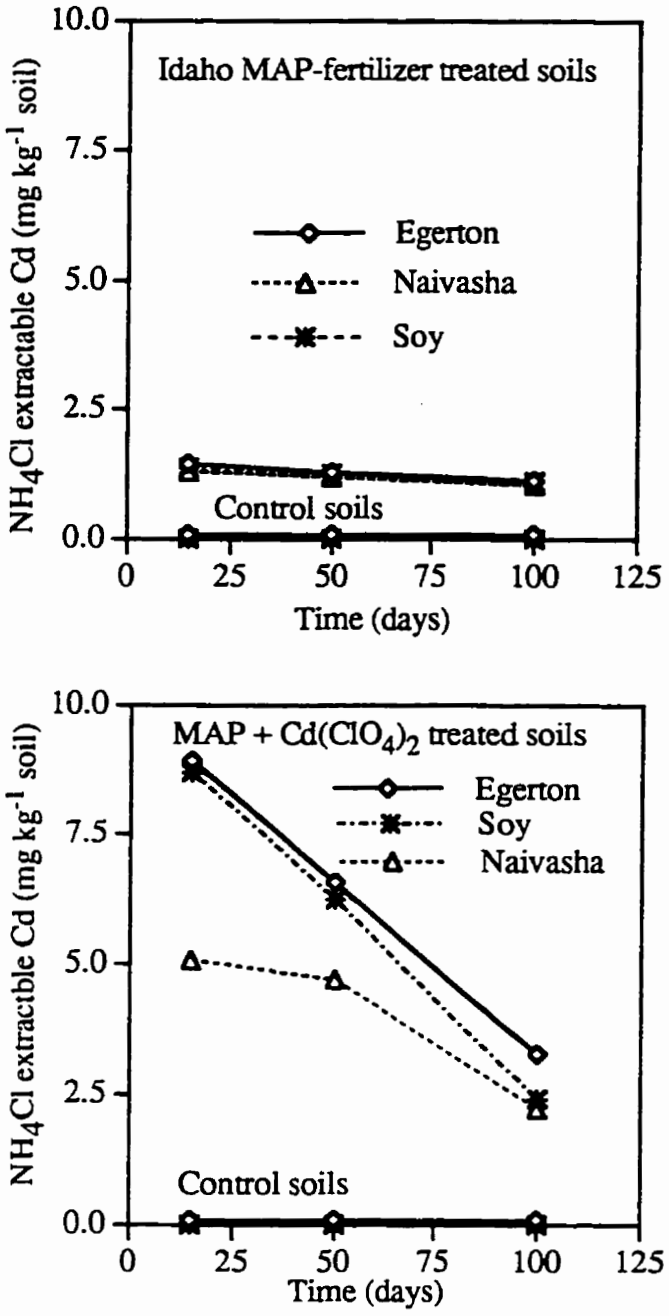

Figure 3.2.3 Effect of incubation time on Cd availability index of the control soils and the soils treated with the Idaho monoammonium phosphate (MAP)-fertilizer or the cadmium perchlorate-added MAP chemical reagent

Table 3.2.4 Amounts of Cd extracted by AAAc-EDTA and NH_4Cl solutions from the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent

Soil treatment	Soils					
	Egerton		Naivasha			
	AAAc-EDTA†	NH_4Cl‡	AAAc-EDTA	NH_4Cl		
	mg Cd kg^{-1} soil				$LSD_{0.05}$	$LSD_{0.01}$
Control	0.14	0.09	0.10	0.05	0.01	0.02
Idaho MAP-fertilizer	1.43	1.13	2.35	1.04	0.08	0.12
MAP chemical + $Cd(ClO_4)_2$	5.06	3.28	3.82	2.22	0.09	0.19
$LSD^{¶}_{0.05}$	0.13	0.11	0.07	0.05		
$LSD^{¶}_{0.01}$	0.28	0.25	0.18	0.11		

† 0.02 M AAAc-EDTA solution

‡ 1 M NH_4Cl solution

¶ LSD values for the amounts of AAAc-EDTA and NH_4Cl extractable Cd in treated soils

hydrous oxides and clays could play a vital role in Cd retention in soils. It has been reported that in acidic soils, the organic matter and sesquioxides may largely control Cd solubility (Kabata-Pendias and Pendias, 1992).

Many investigators have demonstrated that the ease of extraction of applied nutrients and other elements becomes increasingly difficult with increasing periods of reaction with soils (Mann and Ritchie, 1994; Barrow, 1987). This is often termed 'fixation ' although the process is not irreversible as the name implies, merely that the rate of desorption is slower than the rate of adsorption (Barrow, 1987). The increased retention of added metal ions has been attributed to reactions within the surface layer or inside the structure of minerals. The slow diffusion of heavy metals into the structure of minerals as was observed by Brummer et al. (1988) in goethite could explain why ions added to soils become increasingly difficult to desorb and become less available with time. The adsorptive surfaces of sesquioxides which are common in tropical soils and their organic complexes also should be important in Cd retention in the soils studied.

The role of soil microorganisms in the retention and bioaccumulation of heavy metals in soils is well recognized (Berthelin et al., 1995). The deposition and accumulation of heavy metals in soils can be associated with the biodegradation of the organic ligands of soluble metal-organic complexes (Munier-Lamy et al., 1991). The metal may then be precipitated as hydroxide and/or adsorbed by microorganisms. Cell walls of microorganisms can act as sink for metal ions (Beveridge and Murray, 1976; Tsezos, 1983; Volesky 1990). Sorption of soluble Cd by microorganisms in competition with other soil constituents has been investigated using dead and living cells of microorganisms. The removal of Cd^{2+} from a liquid medium by dead bacteria was greater than by live bacteria, clay (montmorillonite) or sand (Kurek et al., 1982), indicating that Cd can be incorporated onto the cell walls of bacteria. Studies on the extraction of metals sorbed on microorganisms have shown that metals appear to be strongly fixed by fungal

cell constituents, particularly cell wall (Berthelin, 1989) that contain chemical compounds such as chitin that bind Cd (Tsezos, 1983).

In studies of the phytoavailability of Cd in triple superphosphate (TSP) and diammonium phosphate (DAP), Mortvedt and Osborn (1982) compared Cd uptake from these fertilizers with known Cd compounds and concluded that Cd in phosphate fertilizers has similar phytoavailability to $Cd(H_2PO_4)_2$ or $CdHPO_4$, or a mixture of these salts. Since the main P constituent in TSP is $Ca(H_2PO_4)_2$, and in DAP is $(NH_4)_3PO_4$, Cd analogues of these P compounds would be predicted to form during the manufacture of TSP and DAP fertilizers. The studies, therefore, suggest that the chemical form of Cd contained in the P-fertilizer, e.g., Idaho MAP-fertilizer may be $Cd(H_2PO_4)_2$, $CdHPO_4$, or a mixture of these salts, which are Cd analogues of the P compounds in commercial P fertilizers.

The reactions responsible for Cd retention in soils are dependent upon soil components and each soil component will be influenced by a number of factors, e.g., soil type, pH, rainfall, temperature, time, management practices and the source of applied Cd (Mann and Ritchie, 1994). It has been reported that phosphates appear to be one of the controlling factors in Cd movement in soil (Levi-Minzi and Petruzzeli, 1984). The solubility product constants of $Cd_3(PO_4)_2$ and $Cd(OH)_2$ are 2.5×10^{-33} and 2.5×10^{-14}, respectively (Dean, 1992). However, according to Street et al. (1978), Cd minerals $Cd_3(PO_4)_2$ and $Cd(OH)_2$ appear to be too soluble to be involved in the precipitation of Cd in soils, except ephemerally in the vicinity of fertilizer granules (Lindsay, 1979).

3.2.3.3 Cadmium distribution in different particle size fractions

At the end of an 100-day incubation period, the control and treated soils were dispersed by sonification by the method of Krishnamurti and Huang (1987). The Cd content of the different particle size fractions was then determined. The amounts of Cd in different particle size fractions were calculated based on the weight of soil , i.e., mg Cd

kg^{-1} soil (Table 3.2.5). In the natural soils, the Cd was predominantly present in the clay fraction of the soils. In the case of the added Cd (62.4 mg kg^{-1}) to the soils, the clay fraction retained the highest proportion of the Cd added (Table 3.2.5). However, the silt and the sand fractions also retained substantial amounts of Cd. When Cd was added to soil, partitioning into various mineral fractions occurred. It took time for the Cd to distribute itself into different mineral fractions. The presence of some reactive components in the silt and sand fractions, e.g., organic matter and sesquioxides would bind Cd. This accounts for the retention of the added Cd in the silt and sand fractions of the soils. The percent distribution of Cd in the various particle size fractions of the soils studied are shown in Figure 3.2.4. The percent distribution is based on the total Cd in the soils. The clay fraction contained the largest proportion of the total Cd. It has also been reported that clays are the major reactive components of many soils and are capable of adsorbing heavy metal ions (Pickering, 1980). The sorption of Cd in soils can be further explained by the hard-soft-Lewis acid-base (HSAB) principle (Alloway, 1995). The HSAB principle states that hard Lewis acids prefer to complex or react with hard Lewis bases and soft acids prefer to complex or react with soft bases (Puls and Bohn, 1988). Most cations are Lewis acids and most anions are Lewis bases. Hard ion indicates high electronegativity, low polarizability and small ionic size, while the opposite is true for soft ions (Puls and Bohn, 1988). Soil clay minerals seem to behave as soft bases (Sullivan, 1977). Sullivan (1977) reported that kaolinite surface functional groups are relatively soft Lewis bases. Cadmium is a soft Lewis acid and will therefore react readily with soft Lewis bases. The HSAB principle has been applied to soils before (Sposito, 1977). Kaolinite and other minerals, e.g., oxides and oxyhydroxides of Al, Fe and Mn were present in the soils studied (Appendices 6.3, 6.4 and 6.5). Kaolinite is a relatively soft Lewis base due to its hydroxyl edge surface functional groups (Puls and Bohn, 1988). The Al and Fe oxides are also soft Lewis bases due to their hydroxyl edge surface functional groups. The hydroxyl edge sites of kaolinite and the reactive sorption sites of Al and Fe oxides

Table 3.2.5 Cadmium content of different particle fractions of the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent at the end of an 100-day incubation period

Treatment	Egerton soil			Naivasha soil			Soy soil				
	Size fractions										
	< 2µm	2-50 µm	> 50 µm	< 2 µm	2-50 µm	> 50 µm	< 2 µm	2-50 µm	>50 µm	$LSD_{0.05}$	$LSD_{0.01}$
	mg kg^{-1} soil										
Control	0.10	0.05	0.00	0.09	0.02	0.00	0.02	0.00	0.00	0.01	0.02
Idaho MAP†-fertilizer	27.6	22.9	11.9	25.5	20.7	16.2	30.6	18.0	13.7	0.7	1.5
MAP chemical + $Cd(ClO_4)_2$	36.7	23.0	2.7	35.5	22.2	4.7	38.3	20.4	3.7	0.1	0.3
$LSD^{¶}_{0.05}$	0.2	0.2	0.1	0.3	0.2	0.2	0.2	0.2	0.2		
$LSD^{¶}_{0.01}$	0.4	0.5	0.2	0.6	0.3	0.3	0.3	0.4	0.4		

† Monoammonium phosphate

¶ LSD values for the Cd content of particle fractions in the treated soils

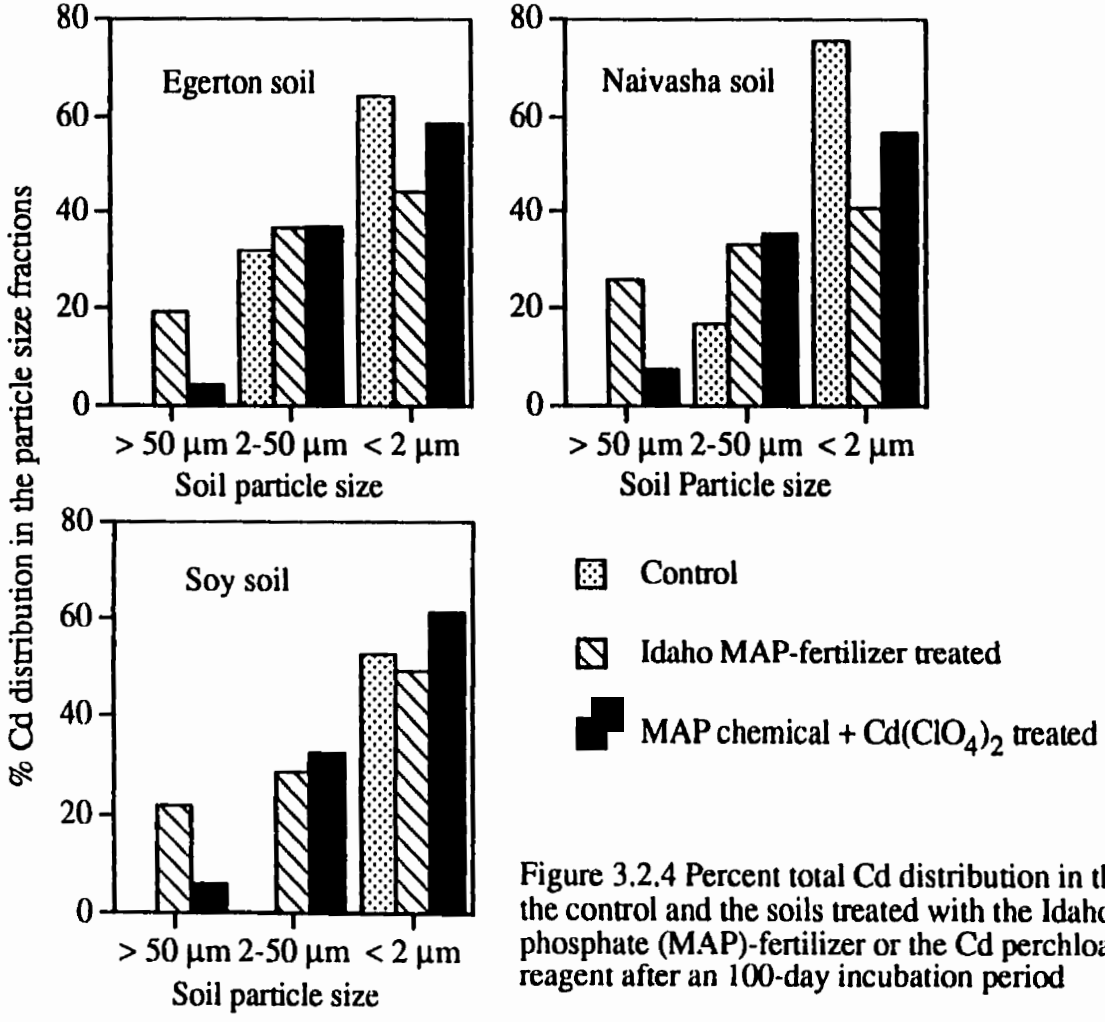

Figure 3.2.4 Percent total Cd distribution in the particle size fractions of the control and the soils treated with the Idaho monoammonium phosphate (MAP)-fertilizer or the Cd perchloarte-added MAP chemical reagent after an 100-day incubation period

(Appendices 6.3, 6.4 and 6.5) appear to adsorb soft Lewis acids, e.g., Cd (Puls and Bohn, 1988). In the tropical soils studied, sesquioxides and their complexes with organics could be the most important reactive soil components in Cd sorption.

The speciation of particulate-bound Cd species in the clay size fractions of the Egerton and Naivasha soils treated with the Idaho MAP fertilizer or the Cd perchlorate added MAP chemical reagent was investigated at the end of an 100-day incubation period using sequential extraction procedure of Krishnamurti et al. (1995a). The amounts of individual particulate-bound Cd species in the clay size fractions are presented in Table 3.2.6. The amounts of particulate-bound Cd species varied with the soil types and the form of Cd introduced to soils (Table 3.2.6). The data showed that the metal-organic complex was the most predominant Cd species and on average accounted for 35.7% of the total Cd in the clay fraction of the soils treated with the Idaho MAP-fertilizer and 54.1% in the clay fraction of the soils treated with the Cd perchlorate-added MAP chemical reagent (Figure 3.2.5).

3.2.4 Summary and conclusions

Transformation of Cd introduced to soils has an impact on Cd speciation and bioavailability. Speciation studies showed that Cd introduced to the soils through the addition of the Idaho MAP fertilizer or the Cd perchlorate added MAP chemical reagent transformed to a series of particulate-bound Cd species. Changes in individual particulate-bound Cd species with time in the treated soils showed that except for the residual Cd species which steadily increased with the incubation time, the rest of the particulate-bound Cd species decreased with time. The metal-organic complex bound-Cd was the most predominant Cd species and on the average accounted for 34.4% of the total Cd in the control soils, 35.6% in the soils treated with the Idaho MAP-fertilizer and 47.8% in the soils treated with the Cd perchlorate-added MAP chemical reagent.

Table 3.2.6 Amounts of particulate-bound Cd species in the clay size fraction of the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent at the end of an 100-day incubation period

Soil	Treatment	Cd content in clay‡	Particulate-bound Cd species†									
			Exch.	Carb.	MOC	Org.	ERMO	AMC	CFeO	Resid.		
		mg kg^{-1}	mg of Cd kg^{-1} soil								$LSD_{0.05}$	$LSD_{0.01}$
Egerton	Idaho MAP‡‡-fertilizer	27.62	0.23	Nd§	10.32	9.27	1.03	0.63	2.02	4.12	0.11	0.20
	MAP chemical + $Cd(ClO_4)_2$	36.70	0.21	Nd	21.16	8.10	2.34	0.52	2.13	2.23	0.12	0.24
Naivasha	Idaho MAP-fertilizer	25.50	0.18	Nd	8.95	7.89	2.02	0.91	2.12	3.42	0.07	0.18
	MAP chemical + $Cd(ClO_4)_2$	35.54	0.25	Nd	17.96	7.32	3.42	1.24	2.79	2.96	0.09	0.21
$LSD_{0.05}$			0.02		0.12	0.11	0.10	0.05	0.08	0.10		
$LSD_{0.01}$			0.03		0.28	0.25	0.22	0.11	0.17	0.25		

† Exch.: exchangeable; Carb.: carbonate-bound; MOC: metal-organic complex bound; Org : organic-bound; ERMO: easily reducible metal oxide-bound; AMC: amorphous mineral colloid-bound; CFeO: crystalline iron oxide-bound, and Resid: residual

‡ Total Cd in the clay size fraction determined by HF-$HClO_4$ digestion method (Jackson, 1958)

‡‡ Monoammonium phosphate

§ Nd - not detectable

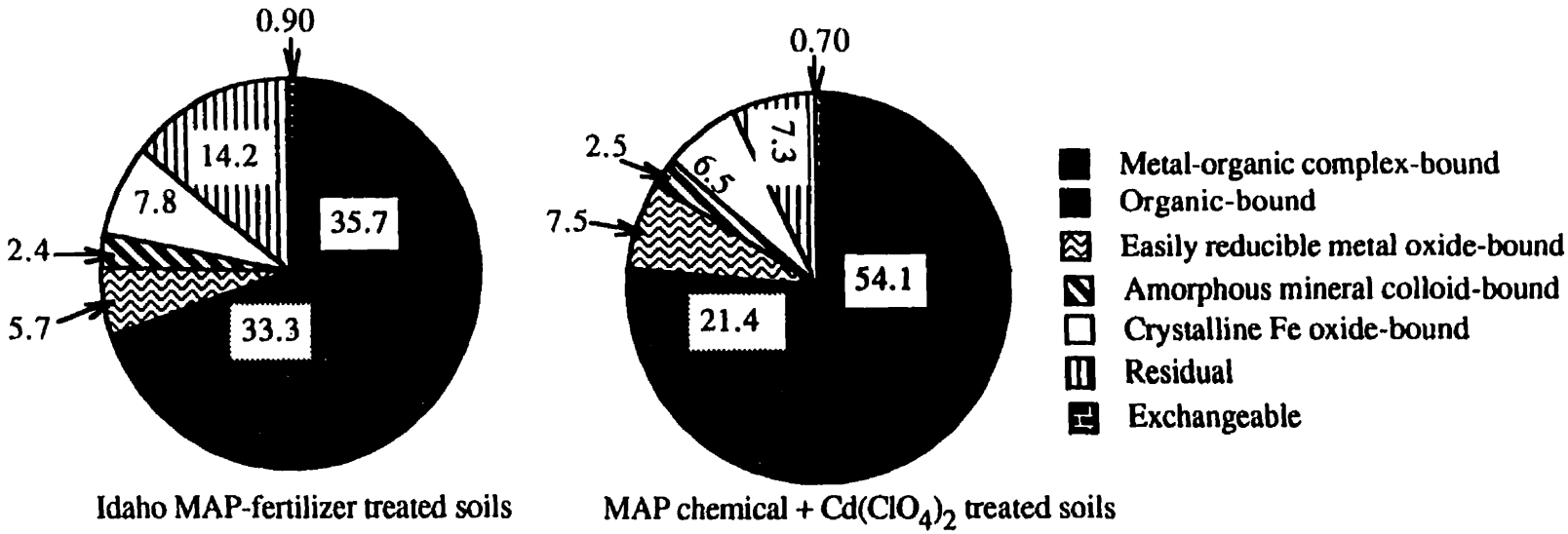

Figure 3.2.5 Average percent distribution of particulate-bound Cd species in the clay size fractions of the soils treated with the Idaho monoammonium phosphate (MAP)-fertilizer or the Cd perchlorate-added MAP chemical reagent after an 100-day incubation period

Metal-organic complex bound-Cd was also the most predominant, compared to other particulate-bound Cd species in the clay size fractions of the soils treated with the Idaho MAP fertilizer or the Cd perchlorate added MAP chemical reagent. Most of the total soil Cd was found in the clay size fraction of the natural and the treated soils, however, silt and the sand fractions also retained appreciable amounts of Cd.

The amounts of M NH_4Cl extractable Cd from the soils treated with the Idaho MAP fertilizer or the Cd perchlorate-added MAP chemical reagent decreased with incubation time. The Cd introduced to soils was transformed with time to less soluble forms, the extent of the transformation depends upon the type of soil.

The M NH_4Cl extracted more Cd from the soils treated with the Cd perchlorate added MAP chemical reagent than from the soils treated with the Idaho MAP fertilizer. The Cd as impurities present in phosphate fertilizer could have reacted with the soil components accounting for the slow release of extractable Cd with time.

The effect of time on retention may have important implications for Cd uptake by plants and hence Cd contamination to the food chain. If Cd is transformed to less available forms with time, there will be less danger of its uptake by plants. However, the residual effect of accumulated Cd in soils as influenced by farming practices should not be overlooked.

3.3 Kinetics of Cadmium Release from Selected Soils by Low-Molecular-Weight Organic acids

3.3.1 Background

Organic acids alter chemical processes in soils through complexation reactions with metals in solution and ligand-exchange reactions at soil surfaces (Stumm, 1986; Martell et al., 1988). Organic acids also retard the formation of crystalline soil minerals containing Al and Fe (Huang and Violante, 1986). Interest in the effects of organic acids on solubility and speciation of metals such as Pb, Cd, and Al has recently increased due to

concerns on environmental issues connected to sludge application to agricultural soils (McColl and Pohlman, 1986; Tam, 1987).

In order to understand the availability and toxicity of trace metals to plants, it is important to assess their mobility in soils. It has been reported that the mobility of trace metals depends on their speciation, which can be assessed using sequential selective extraction procedures (e.g., Tessier et al., 1979; Krishnamurti et al., 1995a). Heavy metal fixation or release can be conventionally represented as follows by the equilibrium reaction (Krishnamurti et al., 1997a):

$$S_f\,Me\ (soil) + H^+\ (solution) \Leftrightarrow S_f\,H\ (soil) + Me\ (solution)$$

where S_f represents the different soil compartments responsible for the fixation of the trace metal, Me. The equation explains the well known effect of acidity on mobility of heavy metals.

To understand the release of heavy metals from soil into soil solution and their subsequent uptake by plants, it requires knowledge of the processes by which metals are transferred to plant roots in the rhizosphere (Nye and Tinker, 1977; Cushman, 1982). The release of root exudates may influence nutrient solubility and uptake indirectly through their effects on microbial activity, rhizosphere physical properties and root growth patterns, and directly by acidification, chelation, precipitation and oxidation-reduction reactions (Uren and Reisenauer, 1988).

A wide variety of low-molecular-weight organic acids (LMWOAs) have been identified in the soil rhizosphere, including oxalic, citric, acetic, malic, succinic, fumaric, etc. (Huang and Schnitzer, 1986; Szmigielska et al., 1995; 1997). These acids are capable of forming complexes with metal ions (Rovira, 1969; Rovira and McDougall, 1967; Stevenson and Fitch 1986; Robert and Berthelin, 1986). Some of these organic acids have been detected in root exudates of certain cereal crops, with the actual amount depending on the crop species (Stevenson, 1967, Cieslinski et al., 1997).

There is some evidence that low-molecular-weight organic acids secreted by plant

roots may lead to the formation of soluble complexes and chelates (Benjamin and Leckie, 1981; Chubin and Street, 1981; Merckx et al., 1986; Mench and Martin, 1991) and may modify the mobility of heavy metals in the rhizosphere (Godo and Reisenauer, 1980; Zang et al., 1991). Alloway (1990) reported that the mobility and bioavailability of Cd is influenced by its speciation, adsorption or coprecipitation onto hydrous metal oxides, complexation with organic components of the root exudates and microbial metabolites. The soluble organic acid ligands in soil solution can introduce a series of equilibria which may modify the fixation and mobility of heavy metals in the soil according to the following equation:

$$S_f\,Me\ (soil) + H^+ + L\ (solution) \quad \Leftrightarrow \quad S_f\,H\ (soil) + MeL\ (solution)$$

where S_f represents the different soil compartments responsible for the fixation of the trace metal, Me is the heavy metal and L is the soluble organic acid ligand.

The specific organic acids present and their concentrations determine the degree to which soil processes are affected. It has been reported that concentrations of organic acids in soil solution are in the range of 1×10^{-3} to 4×10^{-4} M (Stevenson and Ardakani, 1972; Stevenson, 1994). However, higher concentrations ($> 10^{-3}$ M) of LMWOAs have been reported in localized zones at the contact with living organisms (Wang et al., 1967; Robert and Berthelin, 1986). Rhizospheric reactions are known to play an important role in micronutrient acquisition (Curl and Truelove, 1986). High amounts of LMWOAs would be expected to be produced in localized zones where biological activity is intense such as the rhizosphere (Rovira, 1969; Stevenson, 1991) and near decomposing plant residues (Bruckert, 1970; Bruckert and Jacquin, 1969). Lynch et al. (1980) reported that roots and leaves decomposing in soil generate relatively large amounts of acetic, propionic and butyric acids. The concentration of LMWOAs at the immediate root-soil interface would be expected to be high, and hence the use of 2×10^{-2} M and 2×10^{-3} M LMWOAs to study the release of Cd from soils is justified. Organic acids such as citric and oxalic, which form stable complexes with metals, will have a greater impact on metal

solubilization than those that do not form stable complexes (Krishnamurti et al., 1997a). Organic acids are ubiquitous at the soil-root interface in all agricultural soils; however, little attention has been paid to the dynamics of Cd release by low-molecular-weight organic acids from tropical soils.

The objective of this study was to investigate the effect of some low-molecular-weight organic acids (LMWOAs), namely, acetic, citric, fumaric, malic, oxalic and succinic on kinetics of Cd released from selected tropical soils in the main agricultural areas in Kenya.

3.3.2 Materials and methods

Three surface soil samples (Egerton - Andisol, Naivasha - Inceptisol and Soy - Oxisol) (Table 3.1.1) varying widely in physicochemical properties (Table 3.12) were used in this study. The three soils were chosen on the basis of their Cd contents and parent materials. The Egerton soil is derived from volcanic ash and pyroclastic rocks. The Cd content of surface Egerton soil was 0.157 mg kg^{-1} soil. The Naivasha soil (Cd content of 0.119 mg kg^{-1} soil) is derived from lacustrine deposits of volcanic origin whereas Soy soil (Cd content of 0.019 mg kg^{-1} soil) is derived from igneous rocks (Table 3.1.2). The soil samples were air dried and ground to pass through a 2-mm sieve and homogenized before subsequent analysis. Selected properties of these soils are presented in Table 3.1.2.

3.3.2.1 Kinetics of cadmium release from the control and the treated soils

The natural soil samples were incubated with deionized distilled water for 100 days at field capacity. A separate set of soil samples was treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent and incubated for 100 days at field moisture capacity as described in section 3.2.2.1. At the end of the incubation, the natural and treated soil samples were air dried. One gram of each soil sample (natural soil,

after incubation), in duplicate, was placed in a 50-mL polypropylene centrifuge tube and 5 mL of deionized distilled water or 2 x 10^{-2} M of acetic acid, citric acid, fumaric acid, malic acid, oxalic acid or succinic acid was added and then 5 mL of 2 x 10^{-1} M $NaNO_3$ was added to maintain a constant ionic strength of 0.1 M in the system. Acetic, citric, and oxalic acids of concentration of 2 x 10^{-3} M were also used in the study. The LMWOAs were of analytical reagent grade (AnalaR, BDH Inc. chemicals, Toronto, Ont). Two replicates were used in each case. The suspensions were shaken for a predetermined time (0.25, 0.5, 0.75, 1.0, 2.0, 7.0, 15.0 and 24.0 h) at 25 °C in a constant temperature water bath at 60 cycles min^{-1}. At the end of each reaction period, pH was determined with an Accumet Model 825P pH meter (Fisher Scientific, Pittsburgh, PA). No attempt was made to maintain the pH of the system during reaction. At the end of each reaction period, the suspension was passed through a 0.45 μm filter membrane under vacuum. The filtrates were acidified with 0.25 mL of concentrated HNO_3 to eliminate adsorption of Cd onto the walls of the storage tube.

The same procedure as described above was used to investigate the amounts of Cd released to solution by LMWOAs or deionized distilled water from the soils which were treated with the Idaho monoammonium phosphate (MAP)-fertilizer or the Cd perchlorate-added MAP chemical reagent at the end of a 100-day incubation period. Three LMWOAs (acetic acid - monocarboxylic, oxalic acid - dicarboxylic and citric acid - tricarboxylic acid) were used to investigate their effects on Cd release from the treated soils because these organic acids are common in soil environments (Stevenson, 1967) and the Cd complexes with these organic acids have a wide range of the stability constants (Sillen and Martell, 1964). The treated soils were washed once with 10 mL of deionized distilled water to remove free salts prior to their use.

The short reaction period of 0.25 to 1h was used to establish the kinetics of Cd release by LMWOAs from the natural soils and the soils treated with the Idaho MAP-

fertilizer or the Cd perchlorate-added MAP chemical reagent. Selected kinetic models (Sparks, 1989) were used to fit the kinetic data.

Cadmium in the filtrates obtained from the studies of Cd release from the natural and treated soils was determined by using a Perkin Elmer 2280 graphite furnace atomic absorption spectrometer (Norwalk, CT) at 228.8 nm using a pyrolytically-coated tube and L'vov platform. The furnace parameters were the same as those reported earlier in Table 3.1.4.

3.3.2.2. Effect of renewing low-molecular-weight organic acids on cadmium release

The excretion of organic acids in soil rhizosphere by plant roots is a dynamic process. The organic acids released in the rhizosphere would continuously solubilize and mobilize the metals. Hence to simulate this process, the effect of renewing organic acids in the soil solution on Cd release was investigated.

One gram of each soil sample (natural soil or treated soil), in duplicate, was placed in a 50-mL polypropylene centrifuge tube and 5 mL of 2×10^{-2} M LMWOA was added and then 5 mL of 2×10^{-1} $NaNO_3$ was added to maintain a constant ionic strength of 0.1 M in the system. The suspensions were shaken for 2 h at 25 °C in a constant temperature water bath at 60 cycles min^{-1} as was described in Section 3.3.2.1. At the end of the 2-h reaction period the suspensions were centrifuged and then filtered through a 0.45 μm filter membrane under vacuum. The residue on the filter membrane was combined with those at the bottom of the centrifuge tube and fresh LMWOA and $NaNO_3$ added as described above. This treatment was repeated four times. The Cd released to the solution after every 2-h renewal of fresh LMWOAs was determined using graphite furnace atomic absorption spectrometry as stated in section 3.3.2.1.

3.3.3 Results and discussion

3.3.3.1 Amounts of cadmium released from the soils

In the presence of 10^{-2} M LMWAOs, appreciable amounts of Cd were released even at the end of a 15-min reaction period from the natural soils and the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent (Tables 3.3.1 and 3.3.2). No detectable amounts of Cd were released by deionized distilled water from the natural soils at the end of the reaction periods investigated. However, appreciable amounts of Cd were released by deionized distilled water from the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent. The LMWOAs substantially enhanced the Cd released from the soils. The ability of the LMWOAs to release Cd from the soils varied with the nature of the LMWOAs and the soils.

The pH value of the 2 x 10^{-2} M LMWOA solutions used in this study were as follows: oxalic acid 1.88, fumaric acid 2.39, citric acid 2.40, malic acid 2.56, succinic acid 2.84 and acetic acid 3.14. The pH of the soil/LMWOAs suspension for the natural soils was in the order: oxalic acid < citric acid < fumaric acid < malic acid < succinic acid < acetic acid (Table 3.3.1). The Cd released by 10^{-2} M LMWOAs for the natural soils was generally in the order: fumaric acid ≥ citric acid ≥ oxalic acid ≥ malic acid ≥ succinic acid ≥ acetic acid for the natural soils (Table 3.3.1) and citric acid > oxalic acid > acetic acid for the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent (Table 3.3.2).

When the concentration of LMWOAs was 10^{-3} M, detectable amounts of Cd were released from the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent (Table 3.3.3). However, no detectable amounts of Cd were released in the case of the natural soils when the concentration of the LMWOAs was 10^{-3} M. The pH of the 2 x 10^{-3} M LMWOAs used in the study were: acetic acid 3.69; citric acid 3.10 and oxalic acid 2.81. For the Egerton soil treated with the Idaho MAP fertilizer, the Cd released by 10^{-3} M LMWOAs during the 0.25 h reaction period was in the

Table 3.3.1 Soil pH and amount of Cd released from the natural soils at the end of a 15-min reaction period as influenced by 10^{-2} M low-molecular-weight organic acids

Soil†		Low-molecular-weight organic acids							
	DDW‡	Acetic (1.50)‡‡	Citric (3.98)	Fumaric N/A§	Malic (2.36)	Oxalic (3.89)	Succinic (2.10)	$LSD_{0.05}$	$LSD_{0.01}$
	pH								
Egerton	6.0	4.35	3.03	3.11	3.42	2.77	3.82	0.04	0.07
Naivasha	6.8	4.43	3.00	3.19	3.27	2.56	3.74	0.04	0.06
Soy	5.4	3.39	2.69	2.93	2.99	2.39	3.01	0.04	0.07
$LSD_{0.05}$	0.08	0.08	0.05	0.06	0.04	0.06	0.07		
$LSD_{0.01}$	0.19	0.19	0.13	0.15	0.10	0.15	0.17		
	mg Cd kg^{-1} soil								
Egerton	ND¶	0.011	0.026	0.030	0.021	0.023	0.012	0.003	0.007
Naivasha	ND	0.014	0.018	0.021	0.015	0.016	0.014	0.002	0.003
Soy	ND	0.007	0.012	0.013	0.008	0.011	0.007	0.001	0.002
$LSD_{0.05}$		0.002	0.006	0.004	0.002	0.003	0.001		
$LSD_{0.01}$		0.003	0.010	0.007	0.006	0.007	0.003		

† After 100-day incubation with deionized distilled water at the field capacity
‡ Deionized distilled water
‡‡ The log stability constants of Cd-organic ligand complexes in parentheses (Sillen and Martell, 1964) .
§ Not available
¶ Not detectable

Table 3.3.2 Soil pH and amount of Cd released from the treated soils at the end of a 15-min reaction period as influenced by 10^{-2} M low-molecular-weight organic acids

Soil†		Low-molecular-weight organic acids					
		DDW‡	Acetic (1.50)‡‡	Citric (3.98)	Oxalic (3.89)	$LSD_{0.05}$	$LSD_{0.01}$
		pH					
Egerton	Idaho MAP§-fertilizer	5.43	5.41	5.05	4.03	0.04	0.08
	MAP chemical + $Cd(ClO_4)_2$	5.44	4.60	3.67	3.51	0.04	0.07
Naivasha	Idaho MAP-fertilizer	5.04	5.52	5.40	4.32	0.05	0.08
	MAP chemical + $Cd(ClO_4)_2$	5.35	4.80	3.87	3.78	0.04	0.07
Soy	Idaho MAP-fertilizer	5.45	4.37	4.33	3.86	0.06	0.10
	MAP chemical + $Cd(ClO_4)_2$	5.86	4.20	3.27	3.06	0.05	0.09
$LSD_{0.05}$		0.04	0.05	0.05	0.05		
$LSD_{0.01}$		0.07	0.08	0.08	0.07		
		mg Cd kg^{-1} soil					
Egerton	Idaho MAP-fertilizer	0.14	0.24	0.98	0.95	0.02	0.03
	MAP chemical + $Cd(ClO_4)_2$	0.24	0.34	1.20	1.08	0.05	0.09
Naivasha	Idaho MAP-fertilizer	0.13	0.15	0.29	0.18	0.01	0.02
	MAP chemical + $Cd(ClO_4)_2$	0.23	0.26	0.38	0.29	0.01	0.02
Soy	MAP chemical + $Cd(ClO_4)_2$	0.13	0.43	1.24	1.15	0.03	0.05
	Idaho MAP-fertilizer	0.23	0.52	2.44	2.00	0.06	0.11
$LSD_{0.05}$		0.02	0.01	0.04	0.03		
$LSD_{0.01}$		0.03	0.03	0.07	0.05		

† After 100-day incubation with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent at the field capacity

‡ Deionized distilled water

‡‡ The log stability constants of Cd-organic ligand complexes in parentheses (Sillen and Martell, 1964)

§ Monoammonium phosphate

Table 3.3.3 Soil pH and amount of Cd released from the natural and treated soils at the end of a 15-min reaction period as influenced by 10^{-3} M low-molecular-weight organic acids

Soil†		Low-molecular-weight organic acids					
		DDW‡	Acetic (1.50)‡‡	Citric (3.98)	Oxalic (3.89)	$LSD_{0.05}$	$LSD_{0.01}$
		pH					
Egerton	Control	6.00	4.35	3.03	2.77	0.04	0.07
	Idaho MAP§-fertilizer	5.43	5.55	5.45	5.01	0.05	0.10
	MAP chemical + $Cd(ClO_4)_2$	5.44	4.41	4.33	4.11	0.03	0.07
Naivasha	Control	6.80	4.43	3.00	2.56	0.06	0.10
	Idaho MAP-fertilizer	5.04	5.62	5.51	5.22	0.04	0.09
	MAP chemical + $Cd(ClO_4)_2$	5.35	5.20	4.93	4.42	0.04	0.08
Soy	Control	5.40	3.39	2.69	2.39	0.05	0.09
	Idaho MAP-fertilizer	5.45	5.32	5.40	4.16	0.05	0.09
	MAP chemical + $Cd(ClO_4)_2$	5.86	4.34	4.20	3.86	0.04	0.07
$LSD_{0.05}$		0.05	0.04	0.05	0.06		
$LSD_{0.01}$		0.08	0.08	0.09	0.09		
		mg Cd kg^{-1} soil					
Egerton	Control	ND¶	ND	ND	ND		
	Idaho MAP-fertilizer	0.14	0.10	0.31	0.26	0.01	0.02
	MAP chemical + $Cd(ClO_4)_2$	0.24	0.21	0.41	0.38	0.02	0.03
Naivasha	Control	ND	ND	ND	ND		
	Idaho MAP-fertilizer	0.13	0.12	0.25	0.13	0.01	0.02
	MAP chemical + $Cd(ClO_4)_2$	0.23	0.24	0.34	0.25	0.02	0.03
Soy	Control	ND	ND	ND	ND		
	MAP chemical + $Cd(ClO_4)_2$	0.13	0.21	0.38	0.36	0.01	0.03
	Idaho MAP-fertilizer	0.23	0.30	0.58	0.40	0.03	0.05
$LSD_{0.05}$		0.02	0.03	0.02	0.02		
$LSD_{0.01}$		0.03	0.06	0.04	0.04		

† After 100-day incubation with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent at the field capacity

‡ Deionized distilled water

‡‡ The log stability constants of Cd-organic ligand complexes in parentheses (Sillen and Martell, 1964)

§ Monoammonium phosphate

¶ Not detectable

following order: citric acid (0.31 mg kg^{-1} soil) > oxalic acid (0.26 mg kg^{-1} soil) > acetic acid (0.10 mg kg^{-1} soil); for the Egerton soil treated with the Cd perchlorate-added MAP chemical reagent the order was: citric acid (0.41 mg kg^{-1} soil) > oxalic acid (0.38 mg kg^{-1} soil) > acetic acid (0.21 mg kg^{-1} soil). The same trend was observed for the treated Naivasha and Soy soils. The oxalic acid which had the lowest pH did not release more Cd from the treated soils compared to citric acid, indicating that pH was not the dominant factor governing the absolute amount of Cd release in the systems studied. Further, it was observed that more Cd was released by LMWOAs from the soils treated with the MAP chemical plus Cd perchlorate than with the MAP fertilizer (Tables 3.3.2 and 3.3.3). Apparently Cd reacted with certain impurities in the fertilizer thus hindering its release.

In the three soils studied, the Cd release reached a maximum at the end of a 1-h reaction period and then started to fall and approached equilibrium for the natural and the treated soils (Figures 3.3.1 and 3.3.2); the data shown are for the Egerton soil since the other soils followed the same trend. The observed decrease in the amount of Cd released by the LMWOAs with time at the end of 1 h was apparently due to (1) the break down of the soil aggregates caused by agitation which created more surface for the readsorption of the released Cd and/or (2) the readsorption of released Cd by the residual force of the organic ligands adsorbed on soil particles. The Cd of the soil was released to soil solution as Cd-LMWOA complexes. The decrease in the amounts of Cd released by the various LMWOAs from the natural soils at the end of 1 h varied substantially with the type of LMWOAs (Figure 3.3.1). For example, the decrease in the amount of Cd released is more pronounced in the malic acid than in the acetic acid (Figure 3.3.1). Malic acid is a dicarboxylic acid while acetic acid is a monocarboxylic acid. The organic acids can react with the surface of soil particles and this can change the properties of the soil. Compared with acetic acid, malic acid may have the residual carboxyl group after reaction with the soils to bind the Cd released to solution. The release of Cd by LMWOAs was due to

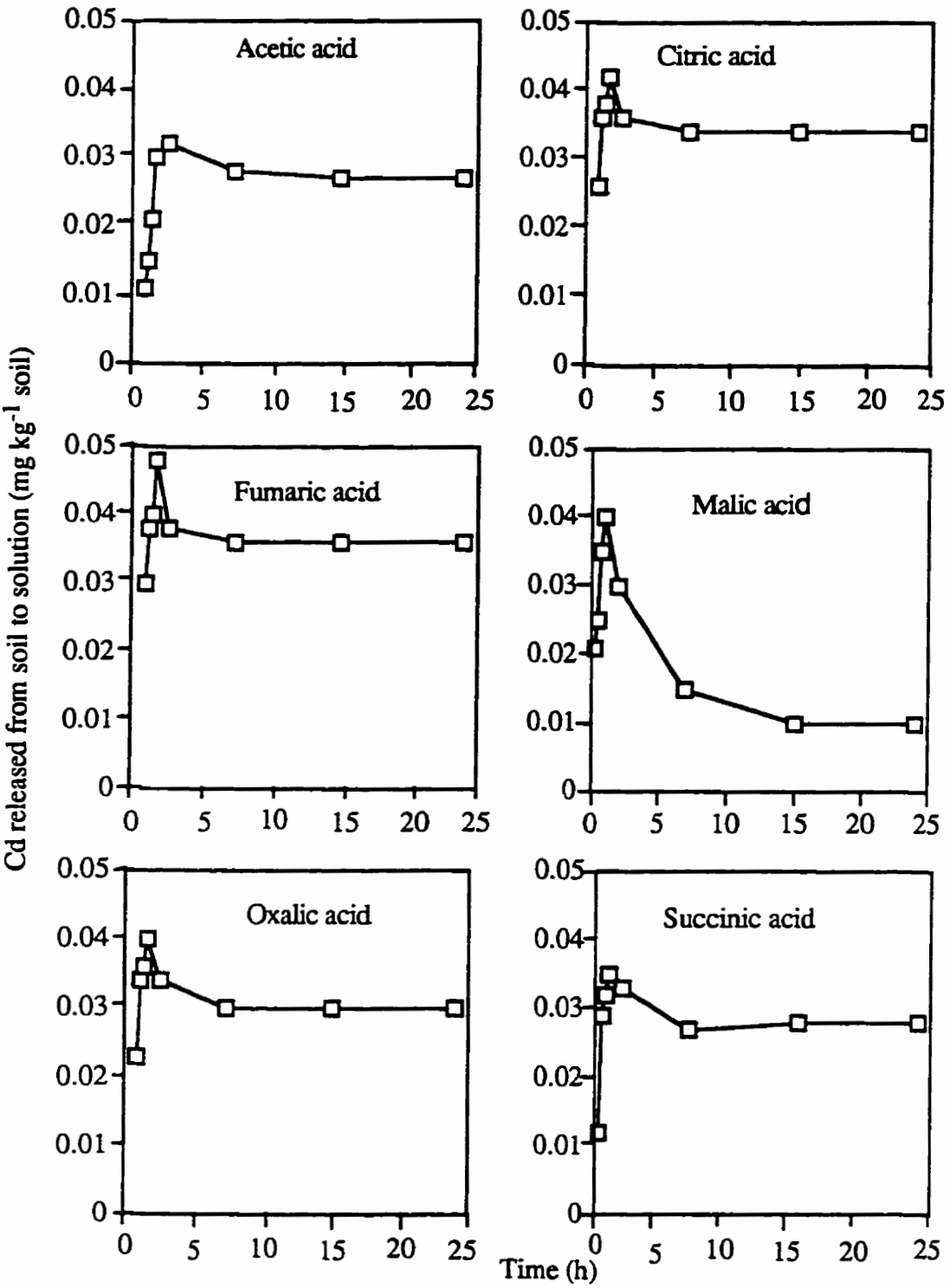

Figure 3.3.1 Changes in the amounts of Cd released by 10^{-2} M low-molecular-weight organic acids from the control Egerton soil during the 0.25 to 24 h-reaction period

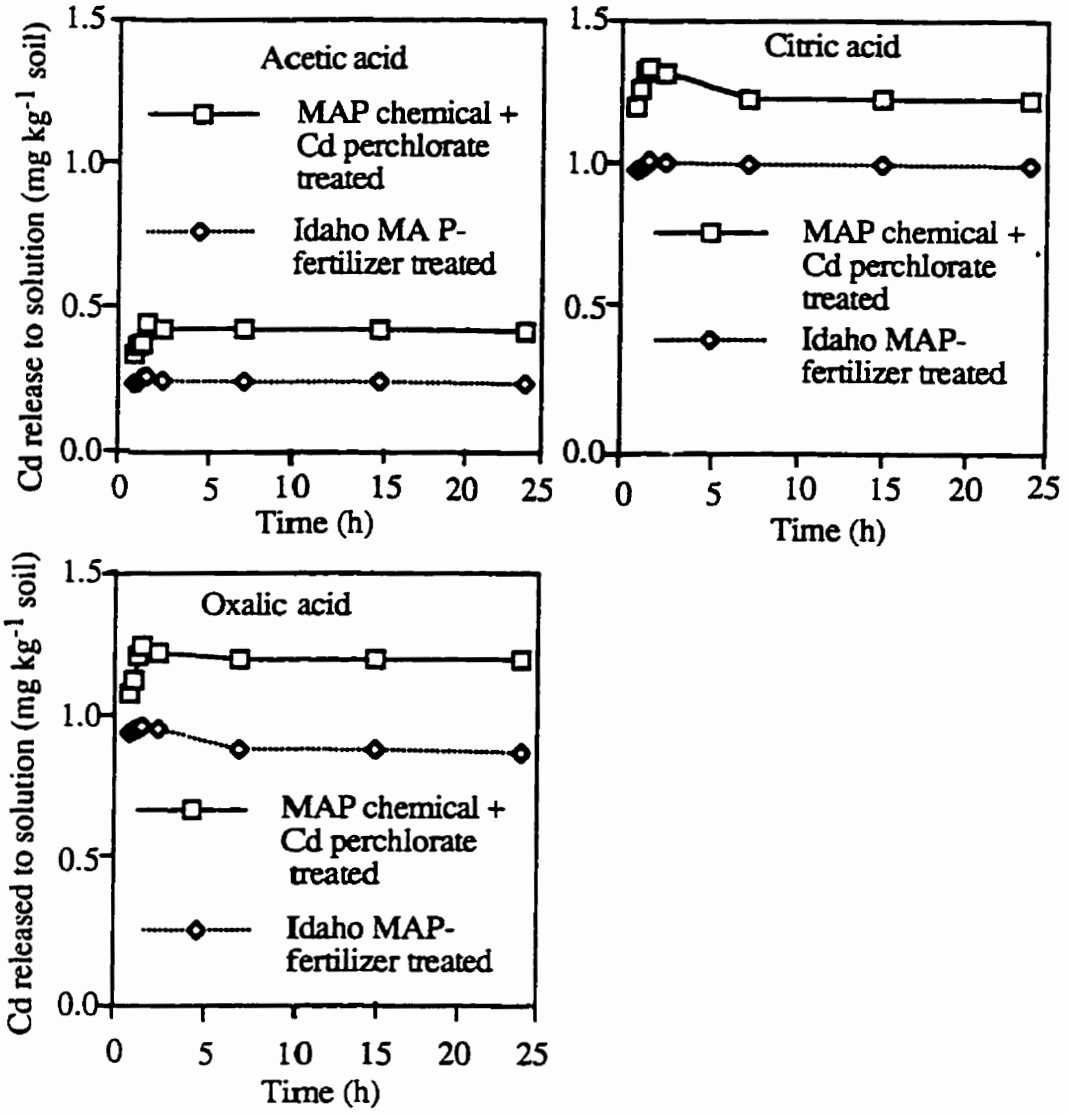

Figure 3.3.2 Changes in the amounts of Cd released by 10^{-2} M low-molecular-weight organic acids during the 0.25 to 24 h-reacton period from the Egerton soil treated with the Idaho monoammonium phosphate (MAP)-fertilizer or the cadmium perchlorate-added MAP chemical reagent.

complexation reaction. The soil particulate-bound Cd was brought into solution by LMWOAs as Cd-LMWOA complexes. The importance of the formation of metal-LMWOA complexes in increasing the solubility of trace elements in the soil rhizosphere has been suggested by various researchers (Merckx et al., 1986; Mench et al., 1988). The significance of the complexation process is clearly reflected in the increase of the amount of the Cd released from the natural soils and the treated soils with the increase in the log stability constants of the Cd-LMWOA (log $K_{Cd\text{-}LMWOA}$) complexes (Sillen and Martell, 1964) as shown in Figure 3.3.3. In the case of the natural surface soils, it was observed that the lowest amount of Cd was released from the Soy soil by the LMWOAs (Figure 3.3.3) which was attributed to its Cd content (Table 3.1.2) and Cd speciation (Table 3.1.7). The metal-organic complex-bound Cd and the organic-bound Cd of the surface horizon of the natural Naivasha and Egerton soils were one order of magnitude higher than those of the Soy soil (Table 3.1.7). However, in the case of the treated soils, the Naivasha soil released the lowest amount of Cd as evidenced in the plot of Cd released to solution versus log K of the Cd-LMWOA complexes (Figure 3.3.3). Apparently the Naivasha soil fixed most of the Cd added and thus limited its release. This could be attributed to the Mn content of the surface horizon of the Naivasha soil which was one order of magnitude higher compared to the Egerton or Soy soil (Table 3.1.2). Heavy metals can be strongly adsorbed on Mn oxides (McKenzie, 1980). The added Cd could have been adsorbed by the Mn oxides present in the Naivasha soil and thus limited the Cd complexation with the LMWOAs (Figure 3.3.3). The treated surface horizon of the Soy soil released the highest amount of Cd compared to the Egerton or the Naivasha soil. The Soy soil is an oxisol and did not fix most of the Cd added. This could be attributed to the low content of the sorptive soil components, e.g., Mn and Fe in the surface horizon of the Soy soil (Table 3.1.2).

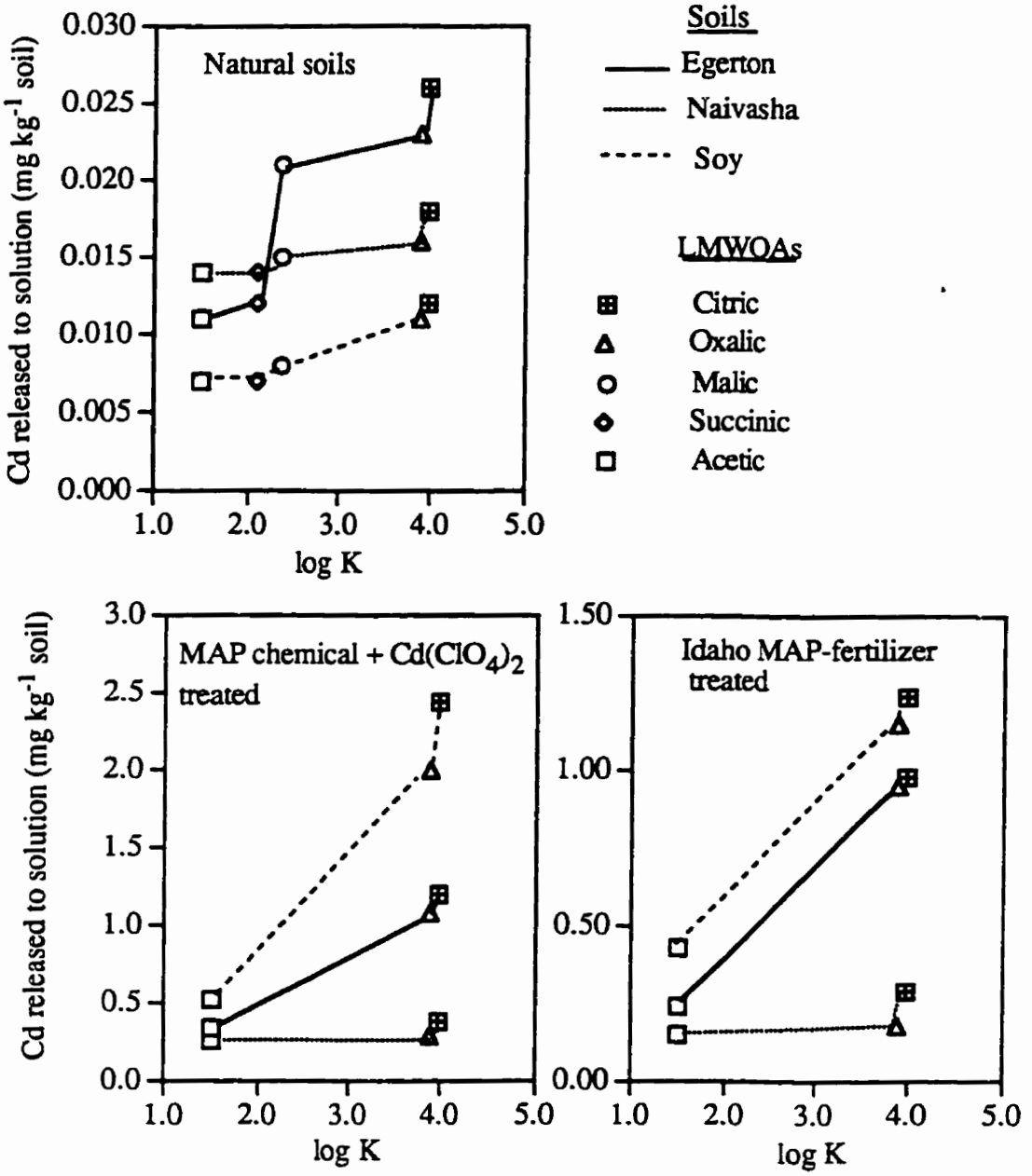

Figure 3.3.3 Relationship between log stability constants (Sillen and Martell, 1964) of the Cd-LMWOA complexes and the Cd released during the 0.25-h reaction period by 10^{-2} M low-molecular-weight organic acids (LMWOAs) from the natural soils and the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent

3.3.3.2 Kinetics of cadmium release

Various kinetic models have been used to fit the data of metal release from the soils according to the methods outlined by Sparks (1989). However, in this study, only three models were examined to fit the data of Cd release from the soils by LMWOAs. The kinetic models examined in this study are presented in Table 3.3.4 .

The reaction period of 0.25 to 1 h was chosen for the kinetic study of Cd release since there was a decrease in Cd release beyond the 1-h reaction period. The degree of fit of each model to the data was evaluated based on the R^2 (determination coefficient), and p value (probability). The choice of kinetic models for describing the release of Cd from the soils was based on these parameters. The closer the R^2 value to 1.0 and the lower the p value the better the model fits the kinetic data. For the kinetic study, absolute amounts (instead of fractions) of the Cd remaining in the sample (Cd_t) or Cd released to solution (Cd_r) were used. The use of absolute amounts is one way to investigate the amounts of Cd released with time. This is more relevant to the amount of Cd entering the food chain.

Table 3.3.4 Kinetic models examined in this study

Model	Linearized equation†
Zero-order kinetics	$Cd_t = a - kt$
1st-order kinetics	$\ln Cd_t = a_1 - k_1 t$
Parabolic diffusion	$Cd_r = a_2 + Dt^{1/2}$

† Cd_t is the amount of Cd remaining in the soil sample at time t; Cd_r is the amount of Cd released to solution from soil at time t; a, a_1 and a_2 are constants in respective equations; k and k_1 are rate constants and D is the overall diffusion coefficient

To establish the kinetics of Cd release, the 0.25 to 1h-reaction period was used to fit the data. In such a short reaction period it was not practicable to investigate the Cd release at more intervals, e.g., every 5 min. Therefore, it is difficult to have more data points. The best fit of a kinetic model to the data is the basis for selection of the best mathematical model to minimize errors in calculation of the rate constants of Cd release from the soils. The parabolic diffusion model was chosen since it was found to fit the Cd release data the best as evidenced from the determination coefficients and p values presented in Tables 3.3.5 (natural soil), 3.3.6 (the soils treated with the Cd perchlorate-added MAP chemical) and 3.3.7 (the Idaho MAP-fertilizer treated soil). The Egerton soil was used as an example to illustrate the degree of fit of each model to the kinetic data of Cd released from the natural soils. The same trend was observed in the other soils. The degree of the fit of the zero order equation to the kinetic data was as poor as $R^2 = 0.613$ and $p = 2.1 \times 10^{-1}$; that of the first order equation was as poor as $R^2 = 0.651$ and $p = 1.9 \times 10^{-1}$ (Tables 3.3.5, 3.3.6 and 3.3.7). A number of researchers have used the parabolic diffusion law to study the kinetics of reactions on soil constituents (Cooke, 1966; Quirk and Chute, 1968; Evans and Jurinak, 1976; Friegenbaum et al., 1981; Jardine and Sparks, 1984; Hodges and Johnson, 1987; Krishnamurti and Huang, 1992, 1993).

The overall diffusion coefficients of the Cd release by LMWOAs calculated from the parabolic diffusion law, which is a measure of the rate of the release of soil Cd to soil solution through complexation with LMWOAs, followed the order: Naivasha > Egerton > Soy for the natural soils (Table 3.3.8). The total Cd content of the surface horizon of the Soy soil was one order of magnitude lower than that of the Naivasha and Egerton soils. The total Cd content of the Egerton soil and the Naivasha soil were in the same order of magnitude (Table 3.1.2). Further, the amounts of the metal-organic complex bound-Cd and organic bound-Cd of the surface horizon of the Naivasha soil and Egerton soil were one order of magnitude higher than those of the Soy soil (Table 3.1.7). This indicates that more Cd would be released from the Naivasha soil than from the Soy soil due to their

Table 3.3.5 The statistical analysis of the kinetic data of Cd release from the natural Egerton soil by 10^{-2} M low-molecular-weight organic acids during the 0.25 to 1 h reaction period

LMWOA†	Kinetic equations‡					
	Zero-order $Cd_t = a - kt$		First-order $\ln Cd_t = a_1 - k_1 t$		Parabolic diffusion $Cd_r = a_2 + Dt^{1/2}$	
	R^2	p	R^2	p	R^2	p
Acetic acid	0.972	1.4×10^{-2}	0.852	7.2×10^{-2}	0.976	1.2×10^{-2}
Citric acid	0.947	2.9×10^{-2}	0.942	2.7×10^{-2}	0.958	2.1×10^{-2}
Fumaric acid	0.878	6.7×10^{-2}	0.876	6.3×10^{-2}	0.929	3.6×10^{-2}
Malic acid	0.949	2.6×10^{-2}	0.939	3.1×10^{-2}	0.951	2.4×10^{-2}
Oxalic acid	0.895	5.4×10^{-2}	0.885	5.9×10^{-2}	0.935	3.3×10^{-2}
Succinic	0.931	3.5×10^{-2}	0.939	3.1×10^{-2}	0.972	1.4×10^{-2}

† Low-molecular-weight organic acids

‡ Cd_t is the amount of Cd remaining in the soil sample at time t; Cd_r is the amount of Cd released to solution from soil at time t; a, a_1 and a_2 are constants in respective equations; k and k_1 are rate constants and D is the overall diffusion coefficient.

Table 3.3.6 The statistical anlysis of the kinetic data for Cd release from the soils treated with the $Cd(ClO_4)_2$ added MAP chemical by 10^{-2} M low-molecular-weight organic acids during the 0.25 to 1 h-reaction period

Soil††	LMWOAs‡‡	Kinetic Equations† Zero-order $Cd_t = a - kt$		1st-order $\ln Cd_t = a_1 - k_1 t$		Parabolic diffusion $Cd_r = a_2 + Dt^{1/2}$	
		R^2	p	R^2	p	R^2	p
Egerton	Acetic	0.821	9.5×10^{-2}	0.870	6.6×10^{-2}	0.874	6.5×10^{-2}
	Citric	0.651	1.9×10^{-1}	0.651	1.9×10^{-1}	0.968	1.5×10^{-2}
	Oxalic	0.778	6.2×10^{-2}	0.780	6.1×10^{-2}	0.876	1.6×10^{-2}
Naivasha	Acetic	0.927	3.6×10^{-2}	0.872	6.5×10^{-2}	0.931	3.4×10^{-2}
	Citric	0.929	3.5×10^{-2}	0.927	3.6×10^{-2}	0.966	1.6×10^{-2}
	Oxalic	0.674	1.7×10^{-1}	0.674	1.7×10^{-1}	0.996	1.0×10^{-3}
Soy	Acetic	0.613	2.1×10^{-1}	0.904	4.9×10^{-2}	0.956	2.2×10^{-2}
	Citric	0.956	2.2×10^{-2}	0.956	2.2×10^{-2}	0.972	1.4×10^{-2}
	Oxalic	0.773	1.2×10^{-1}	0.773	1.2×10^{-1}	0.960	2.0×10^{-2}

† Cd_t is the amount of Cd remaining in the soil sample at time t; Cd_r is the amount of Cd released to solution from soil at time t; a, a_1 and a_2 are constants in respective equations; k and k_1 are rate constants and D is the overall diffusion coefficient.

†† MAP chemical + $Cd(ClO_4)_2$ treated soils

‡‡ Low-molecular-weight organic acids

Table 3.3.7 The statistical analysis of the kinetic data of Cd release from the soils treated with the Idaho MAP-fertilizer by 10^{-2} M low-molecular-weight organic acids during the 0.25 to 1 h reaction period

Soil ††	LMWOA‡‡	Kinetic equations† Zero-order $Cd_t = a - kt$		First-order $\ln Cd_t = a_1 - k_1 t$		Parabolic diffusion $Cd_r = a_2 + Dt^{1/2}$	
		R^2	p	R^2	p	R^2	p
Egerton	Acetic acid	0.935	3.2×10^{-2}	0.931	3.4×10^{-2}	0.952	2.4×10^{-2}
	Citric acid	0.844	8.1×10^{-2}	0.910	4.6×10^{-2}	0.935	3.2×10^{-2}
	Oxalic acid	0.868	2.1×10^{-2}	0.868	2.1×10^{-2}	0.914	1.0×10^{-2}
Naivasha	Acetic acid	0.958	2.1×10^{-2}	0.964	1.8×10^{-2}	0.978	1.2×10^{-2}
	Citric acid	0.960	2.1×10^{-2}	0.966	1.7×10^{-2}	0.984	1.0×10^{-2}
	Oxalic acid	0.947	5.2×10^{-2}	0.948	5.1×10^{-2}	0.968	2.4×10^{-2}
Soy	Acetic acid	0.843	8.1×10^{-2}	0.944	2.8×10^{-2}	0.957	2.1×10^{-2}
	Citric acid	0.962	2.0×10^{-2}	0.960	2.1×10^{-2}	0.978	1.6×10^{-2}
	Oxalic acid	0.607	1.2×10^{-1}	0.604	1.3×10^{-1}	0.968	2.4×10^{-2}

† Cd_t is the amount of Cd remaining in the soil sample at time t; Cd_r is the amount of Cd released to solution from soil at time t; a, a_1 and a_2 are constants in respective equations; k and k_1 are rate constants and D is the overall diffusion coefficient.

†† Idaho MAP-fertilizer treated soils

‡‡ Low-molecular-weight organic acids

differences in Cd content and speciation. The rate of Cd release from each soil varied with the nature of LMWOAs. Compared with acetic acid (log $K_{Cd\text{-}acetic}$ = 1.50), citric acid complexes more strongly with Cd (log $K_{Cd\text{-}citric}$ = 3.98) (Sillen and Martell, 1964). The rate of Cd release was related to the stability of the Cd-LMWOA complexes as was shown earlier by the amounts of Cd released versus the log K of the Cd-LMWOA complexes (Figure 3.3.3).

Table 3.3.8 Overall diffusion coefficients of Cd released from the natural soils by 10^{-2} M low-molecular-weight organic acids during the 0.25 to 1 h reaction period

LMWOAs†	Overall diffusion coefficients				
	Soils‡				
	Egerton	Naivasha	Soy	$LSD_{0.05}$	$LSD_{0.01}$
	mg kg^{-1} $h^{-0.5}$				
Acetic	0.02	0.03	0.01	0.01	0.02
Citric	0.04	0.06	0.01	0.01	0.02
Fumaric	0.06	0.07	0.02	0.01	0.02
Malic	0.02	0.06	0.01	0.01	0.02
Oxalic	0.04	0.06	0.01	0.01	0.02
Succinic	0.03	0.04	0.01	0.01	0.02
$LSD_{0.05}$	0.02	0.01	0.002		
$LSD_{0.01}$	0.03	0.02	0.004		

† Low-molecular-weight organic acids

‡ After 100-day incubation with deionized distilled water at the field capacity

Further, the overall diffusion coefficients of the Cd release by LMWOAs in the treated soils (Table 3.3.9) were substantially higher than those in the natural soils (Table 3.3.8). The rate of Cd released from the treated soils by citric or oxalic acid was significantly higher than that by acetic acid (Table 3.3.9).

Table 3.3.9 Overall diffusion coefficients of Cd released from the treated soils by 10^{-2} M low-molecular-weight organic acids during the 0.25 to 1 h reaction period

Soil	Treatment[†]	Overall diffusion coefficient				
		LMWOA[‡]				
		Acetic	Citric	Oxalic		
		— mg kg^{-1} $h^{-0.5}$ —			$LSD_{0.05}$	$LSD_{0.01}$
Egerton	Idaho MAP[§]-fertilizer	0.05	0.15	0.14	0.02	0.03
	MAP chemical + $Cd(ClO_4)_2$	0.09	0.28	0.23	0.03	0.05
Naivasha	Idaho MAP-fertilizer	0.04	0.12	0.11	0.01	0.02
	MAP chemical + $Cd(ClO_4)_2$	0.05	0.13	0.12	0.01	0.02
Soy	Idaho MAP-fertilizer	0.03	0.14	0.13	0.01	0.02
	MAP chemical + $Cd(ClO_4)_2$	0.06	0.15	0.14	0.02	0.03
$LSD_{0.05}$		0.01	0.02	0.02		
$LSD_{0.01}$		0.02	0.04	0.03		

[†] After 100-day incubation with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent at the field capacity

[‡] Low-molecular-weight organic acids

[§] Monoammonium phosphate

The complexibility of the soil Cd by LMWOAs would be expected to vary with the nature of the particulate-bound Cd species of the soil. The rate of Cd release by each organic ligand apparently varied with the nature of the particulate-bound Cd species of the soils. For example, in the natural soils, the metal-organic complex bound-Cd and organic bound-Cd in the Naivasha soil were one order of magnitude higher than those of the Soy soil (Table 3.1.7). The rate of Cd release from the natural Naivasha soil by LMWOAs were significantly higher compared to the natural Soy soil (Table 3.3.8).

However, the exact nature of the structure of the Cd-LMWOA complexes which are present in soil solution and their effect on the rate of Cd release is yet to be uncovered. The activity of Cd species in the soil solution at the soil-root interface and the potential buffering capacity of the soil for Cd would govern the labile soil Cd.

3.3.3.3 Renewal of Low-molecular-weight organic acids and cadmium release

The effect of renewing LMWOAs on Cd release from the natural and treated soils was investigated by adding fresh LMWOAs after every 2-h reaction period. The organic acids were very effective in continuously releasing Cd from the soils when renewed after every 2 h, indicating the importance of dynamics of LMWOAs in the mobility of Cd at the root-soil interface through the formation of soluble Cd-LMWOA complexes (Figure 3.3.4). Egerton soil was used as an example since other soils followed the same trend. The same trend was also observed in the soils treated with Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent (Figure 3.3.5). The observed trend explains the importance of LMWOAs in mobilizing and solubilizing Cd through complexation reaction in soils. Mench et al. (1988) reported that LMWOAs such as succinic and citric acids were capable of complexing metal cations in the soil rhizosphere.

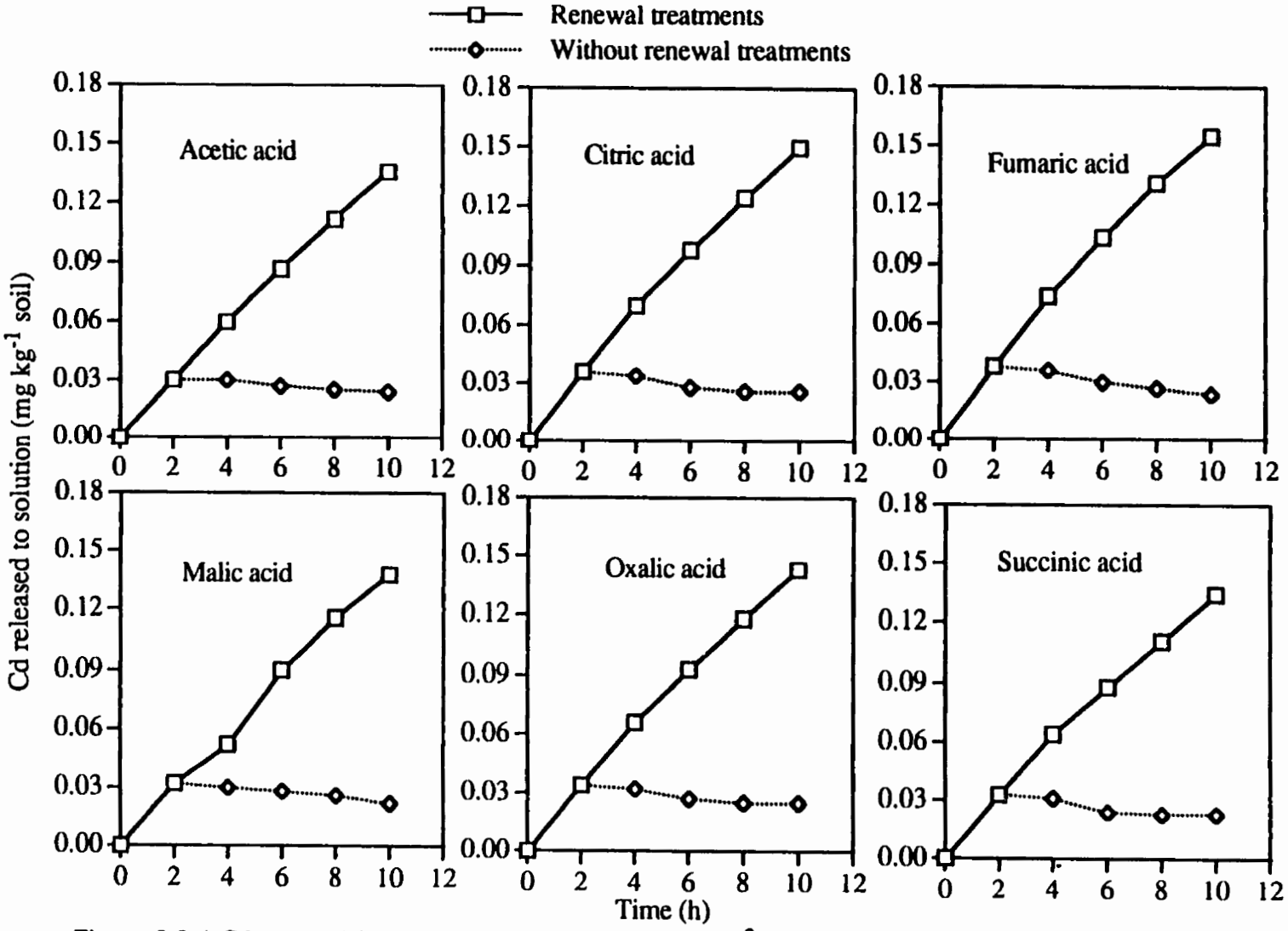

Figure 3.3.4 Cd released from the natural Egerton soil by 10^{-2} M low-molecular weight organic acids

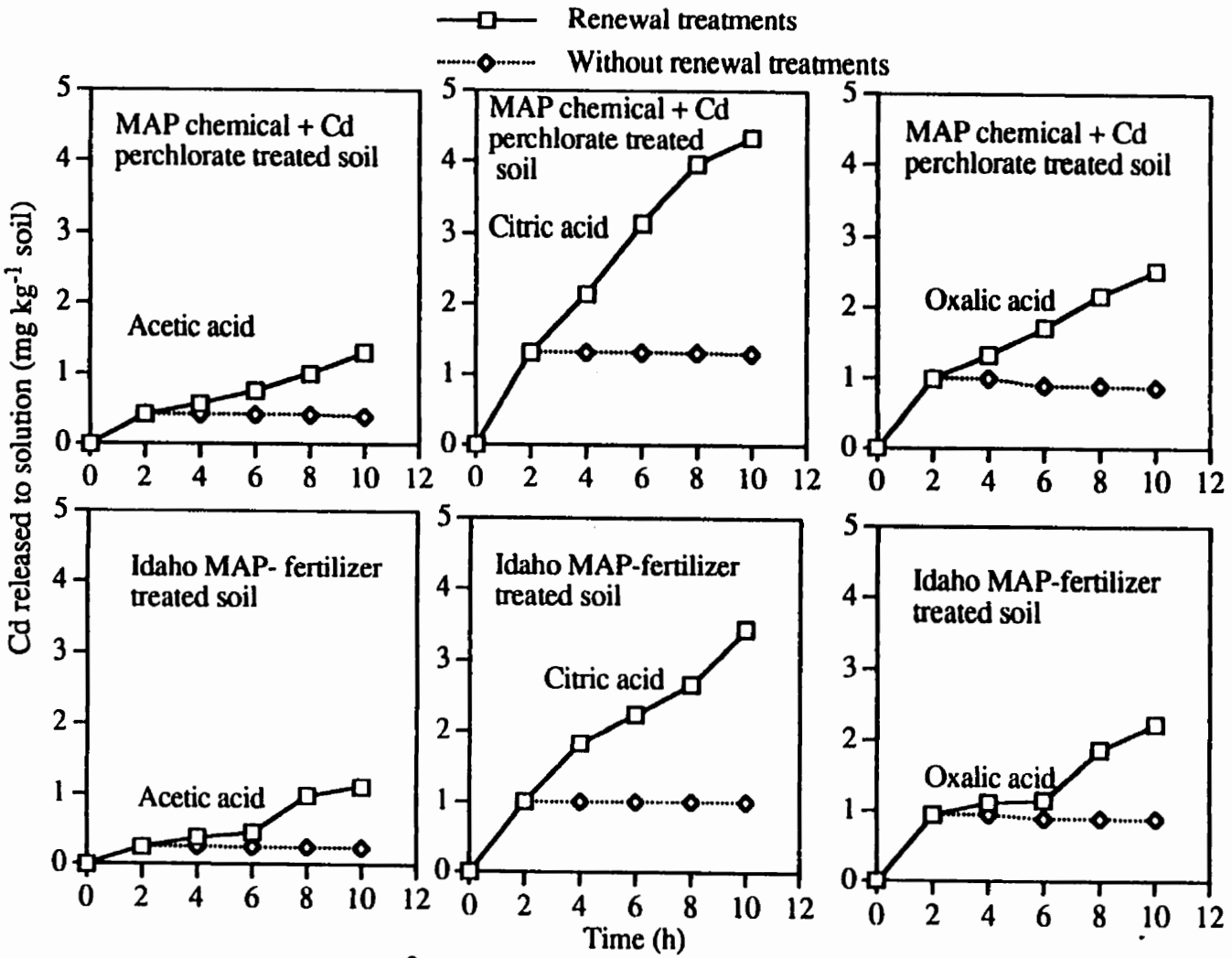

Figure 3.3.5 Cd released by 10^{-2} M low-molecular-weight organic acids from the Egerton soil treated with the Idaho monoammonium phosphate (MAP)-fertilizer or the cadmium perchlorate-added MAP chemical reagent

Complexation of metals in soil disturbs the equilibrium between the labile metal on the solid phase and soil solution and thus enhances the release of the metal to the soil solution. Hence, the formation of metal complexes at the soil-root interface should replenish the metal ion taken up by the plant. Removal of a metal ion by plant uptake thus establishes a concentration gradient to transport more complexed metal toward the root surface. The steady release of Cd upon renewal of LMWOAs indicates the importance of dynamics of LMWOAs in understanding the Cd mobility in the soil rhizosphere.

3.3.4 Summary and Conclusions

The amounts of Cd released by 10^{-2} M LMWOAs from the natural soils or the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent reached a maximum at the end of 1-h reaction period and then started to fall and approached a plateau. The decrease of Cd concentration with time was apparently due to readsorption of released Cd on soil particles or due to break down of the soil particles which created more surface for the readsorption of the released Cd. The 1h period investigated was apparently too short for noticeable microbial degradation of the LMWOAs to occur. When the concentration of LMWOAs was 10^{-3} M, no detectable amounts of Cd were released from the natural soils and appreciable amounts of Cd were released from the treated soils. Further, appreciable amounts of Cd were released even by deionized distilled water from the treated soils.

The amounts of Cd released from the natural soils during the short-term reaction period of 15 min varied with the soil types and generally were in the following order: Egerton (Andisol) > Naivasha (Inceptisol) > Soy (Oxisol). The amount of Cd released from the soil by LMWOAs increased with the log stability constant values of the Cd-LMWOA complexes, indicating that Cd was brought into solution by LMWOAs as Cd-LMWOA complexes. The decrease in the amounts of Cd released by the various

LMWOAs from the natural soils at the end of 1-h reaction period substantially varied with the type of LMWOAs.

The parabolic diffusion equation was chosen as the best mathematical model to describe the short-term kinetics of Cd release from the soils in the presence of LMWOAs. The overall diffusion coefficient values of the Cd release from the natural soils and the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent varied with the soil type and the nature of LMWOAs. The overall diffusion coefficients of the Cd release by LMWOAs were substantially higher in the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent than in the natural soils. This is attributed to the differences in Cd content and speciation.

The release of organic acids from roots would continuously mobilize Cd from the rhizosphere, as indicated by the continued release of Cd upon renewal of LMWOAs after every 2-h reaction period. The continuous release of Cd from the soils by renewal of LMWOAs indicates the sustaining power of the soils to replenish the Cd labile pool of the soils. The results indicate that LMWOAs commonly present in root exudates play a vital role in the mobilization of Cd in the soils and hence may influence its uptake by the plants. The results further indicate that when phosphate fertilizers are applied to soils, the LMWOAs present in the rhizophere would enhance Cd release to the soil solution.

3.4 The Influence of Potassium Chloride on Cadmium Dynamics of Soils

3.4.1 Background

Transformation of soil Cd to available forms is a function of factors like pH, Eh, and microbial activity (Alloway, 1995). Apart from these factors, a number of investigators have reported the effect of chloride on Cd availability (Bingham et al., 1983, 1984; McLaughlin et al., 1994a, b, 1996). Cadmium complexes readily with chloride and this complexation may influence its availability. McLaughlin et al. (1994a) observed elevated Cd concentrations in potato tubers which were grown in predominantly saline

soils and suggested that this was due to the effect of Cl mobilizing Cd within the soil and increasing its availability to plants. Chloride reduces Cd sorption by soil and has been identified as increasing the mobility of Cd through soils (Garcia-Miragaya and Page, 1976; Boekhold et al., 1993). This is ascribed to the formation of Cd-chloride complexes in solution (Hahne and Kroontje, 1973).

It has been reported that soil salinization can be caused by addition of chloride salts in irrigation waters (Jurinak and Suarez, 1990; McLaughlin et al., 1996). Generally the dominant anion in the irrigation water is Cl^- (Jurinak and Suarez, 1990). If the chloride concentrations in soil solution are sufficiently high, significant complexation of chloride with Cd can take place to decrease Cd sorption and increase total Cd concentrations in soil solution. Concentrations of Cl above about 10 mM can lead to over 50% of the inorganic Cd in solution being in the form of Cd-chloride complexes (McLaughlin et al., 1996); however, this will depend on the concentration of Cd in the soil solution. McLaughlin and Tiller (1994) reported that in normal agricultural soils, the effect of salinity on the Cd uptake by plants is due to chloro-complexation of Cd^{2+} releasing sorbed Cd into soil solution. The desorbed Cd (predominantly $CdCl^+$) is then taken up by plants directly or enhances diffusion of Cd^{2+} to the sites of ion uptake (McLaughlin et al, 1996). McLaughlin et al. (1997) recently observed that the concentration of Cd in potato tubers is related to the degree of chloro-complexation of Cd in solution.

Potassium chloride is known to greatly enhance the release of cations like Mn from soils (Krishnamurti and Huang, 1992, 1993; Tu et al., 1995). The adsorption of cadmium onto soil is normally rapid with more than 90% being adsorbed within the first 10 min and an equilibrium is reached in 1 h (Christensen, 1984a). Besides the adsorption of Cd onto soil, its desorption induced by the high concentration of salts through application of potash fertilizers such as KCl in agricultural practices deserves close attention. Potassium chloride fertilizers (muriate of potash) are often applied to K-deficient

tropical soils to supplement the soil supply of K and to avoid soil depletion of this element.

The chemical behavior of Cd in the reaction with soil components was explained by Puls and Bohn (1988) based on the hard-soft Lewis acid-base principle. Cadmium is a soft Lewis acid and would, therefore, react and form complexes most readily with soft Lewis bases, such as chloride (Alloway, 1995). However, little attention has been paid to the influence of potassium chloride fertilizer on Cd release from tropical soils where potassium chloride fertilizer is often used to correct K deficiency. Because of the high concentration of chloride in the immediate vicinity of KCl fertilizer zone, Cd should form a series of complexes with chloride ions, e.g., $CdCl^+$, $CdCl_2^o$, $CdCl_3^-$, and $CdCl_4^{2-}$. Further, monoammonium phosphate (MAP) fertilizers have a wide range of Cd content (8 to 174 mg Cd kg^{-1}) (Kpomblekou and Tabatabai, 1994; Williams and David, 1976). Significant amounts of Cd are present in Idaho monoammonium phosphate fertilizer (144 mg kg^{-1}) (Krishnamurti et al., 1996). The solution concentration of Cd at the phosphate fertilizer granule-soil interface can be as high as 2.8×10^{-3} M (Appendix 6.1). The applied KCl fertilizer may react with solution Cd to form Cd-chloride complexes. The Cd-chloride complexes in the soil solution may be adsorbed or weakly adsorbed onto soil particles. The impact of KCl fertilizer on the dynamics of soil Cd remains to be uncovered. The objective of this study was to investigate the effect of KCl on the dynamics of Cd of selected tropical soils from main agricultural areas in Kenya.

3.4.2 Materials and Methods

Three surface soils, Egerton (Andisol), Naivasha (Inceptisol) and Soy (Oxisol) from the main agricultural areas in Kenya were used in this study. The description of the sampling sites and the parent materials of the soils were presented in Table 3.1.1. The general properties of these soils were presented in Table 3.1.2. The soil samples were air dried and crushed to pass through a 2-mm sieve prior to use.

3.4.2.1 Kinetics of cadmium release from the natural and treated soils

When the KCl fertilizers are applied to soils, the concentration of dissolved Cl ions in the immediate vicinity of fertilizer granules can be higher than 1 M (Sakurai and Huang, 1996). The use of 1 M KCl solution to investigate the potassium chloride induced Mn release from selected temperate and subtropical regions has been reported by Krishnamurti et al. (1992, 1993). In order to simulate the effect of Cl on Cd release from soils in the vicinity of the fertilizer granules, 1.0 M KCl solution was chosen for the kinetic study of the KCl -induced Cd release from the soils.

The natural soil samples and the soil samples treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent were incubated for 100 days at field capacity as described in section 3.2.2.1. One gram of each soil (natural soil, the Idaho MAP- fertilizer treated soil or the soil treated with the Cd perchlorate-added MAP chemical reagent), in duplicate, was placed in a 50-mL polypropylene centrifuge tube and 10.0 mL of 1.0 M of KCl chemical solution or KCl-fertilizer solution was added. The centrifuge tube containing a soil suspension was placed in a water bath shaker at 25°C, with a shaking speed of 60 cycles min^{-1}. At the end of each reaction period (0.25, 0.5, 0.75, 1.0, 2.0, 7.0, 15.0 and 24.0 h), the suspensions were filtered through a 0.45 μm pore-size membrane under vacuum. The pH of the suspensions was monitored at the end of each reaction period. The same procedure was used to investigate the amounts of Cd release by deionized distilled water from the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent.

Cadmium in the filtrates was determined using a Perkin Elmer 2280 graphite furnace atomic absorption spectrometer (Norwalk, CT) at 228.8 nm using a pyrolytically-coated tube. The furnace parameters used in the determination of Cd in the filtrates were the same as those reported earlier in Table 3.1.4. The Cd determined in the filtrates (Cd_r) was the Cd released from the soil during reaction time, t. The Cd remaining in the sample

(Cd_t) at different reaction times was the difference between the total Cd present in the soil samples and the Cd released to solution.

In the field conditions, the concentration of chloride should decrease gradually with increasing distance from the vicinity of the KCl fertilizer applied. In order to investigate the effect of various chloride concentrations on Cd release, 0.10 M KCl chemical or KCl fertilizer and 0.01 M KCl chemical or KCl fertilizer solutions were also used in the study of Cd released from the soils according to the method described above.

3.4.2.2 The adsorption of cadmium by the soils as influenced by potassium chloride

The surface horizons of the Egerton and Naivasha soils were used in this study. One gram (oven dried basis) of the natural soil sample, in duplicate, was placed in a 50-mL polypropylene centrifuge tube and 10.0 mL of 8.89×10^{-4} M (100 ppm Cd) of $Cd(ClO_4)_2 .6H_2O$ solution was added in the absence or presence of 1.0 M or 0.1 M KCl solution. The centrifuge tube containing a soil suspension was placed in a water bath shaker at 25°C, with a shaking speed of 60 cycles min^{-1}. At the end of each reaction period (0.25, 0.5, 0.75, 1.0 and 2.0 h) the suspensions were filtered through a 0.45 μm pore-size membrane under vacuum. Cd remaining in solution at the end of each reaction period was determined in the filtrates as described in Section 3.4.2.1.

3.4.3 Results and discussion

3.4.3.1 Amounts of cadmium released from the soils

The Cd released from the natural soils during the 15-min reaction period as influenced by KCl chemical or KCl fertilizer (muriate of potash) solution varied with the soils (Table 3.4.1). The total Cd content of the Soy soil was one order of magnitude lower than that of the Egerton or the Naivasha soils (Table 3.1.2). Further, the amounts of metal-organic complex bound-Cd and organic bound-Cd of the surface horizons of the

Egerton or the Naivasha soils were one order of magnitude higher than those of the Soy soil (Table 3.1.7). Due to the differences in the Cd content and speciation among these soils, more Cd would be released from the Egerton soil or the Naivasha soil than from the Soy soil. The Cd released from the control soils by deionized distilled water or by 0.01 M KCl chemical or KCl fertilizer solution was not detectable. However, appreciable amounts of Cd were released from the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent by deionized distilled water (Table 3.4.2) or 0.01 M and 0.1 M KCl chemical or 0.01 M and 0.1 M KCl fertilizer solution at the end of the 15-min reaction period (data not shown). The Cd released from the treated soils by M KCl chemical or M KCl fertilizer solution varied with the form of Cd introduced to the soils (Table 3.4.2). This was apparently due to the low Cd solubility in the Idaho MAP-fertilizer treated soils compared with the soils treated with the Cd perchlorate-added MAP chemical reagent. Compared with the natural soils, the amounts of the Cd released from the treated soils by M KCl chemical or M KCl fertilizer were two orders of magnitude higher (Tables 3.4.1 and 3.4.2). This indicates that application of MAP and potash (KCl) fertilizers would significantly enhance the Cd released from the soils. The Cd released by KCl fertilizer from the soils treated with the Cd perchlorate-added MAP chemical reagent was from the Cd perchlorate. The Cd released by KCl fertilizer from the soils treated with the Idaho MAP-fertilizer was from the Cd present as an impurity in the MAP fertilizer. In the treated soils (Table 3.4.2), it was also observed that there was significant differences between the amounts of Cd released by M KCl chemical and M KCl fertilizer. This could be attributed to the impurities in the KCl fertilizer such as Fe oxides which could react with the Cd added to the soil, thus, limiting its release.

The amounts of Cd released from the natural soils or the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent by M KCl chemical or KCl fertilizer increased initially up to a reaction period of 1 h, then slowly decreased with time and tended to reach a plateau (Figure 3.4.1). The decrease was

apparently due to readsorption of released Cd onto soil particles. The Cd released from the treated soils by 0.01 M or 0.1 M KCl chemical or KCl fertilizer during the 0.25 to 1 h-reaction period followed the same trend (data not shown).

Table 3.4.1 Amount of Cd released from the natural soils by 1 M KCl chemical or KCl fertilizer solution at the end of a 15-min reaction period

Soil†	1 M KCl chemical solution		1 M KCl fertilizer solution					
	pH	Cd‡	pH	Cd	pH		Cd	
					$LSD_{0.05}$	$LSD_{0.01}$	$LSD_{0.05}$	$LSD_{0.01}$
		mg kg^{-1} soil		mg kg^{-1} soil				
Egerton	5.57	0.05	5.55	0.05	0.03	0.05	0.01	0.02
Naivasha	6.39	0.03	6.34	0.03	0.04	0.07	0.01	0.02
Soy	4.83	0.01	4.71	0.01	0.07	0.13	0.01	0.02
$LSD_{0.05}$	0.05	0.01	0.07	0.01				
$LSD_{0.01}$	0.09	0.02	0.14	0.02				

† After incubation with deionized distilled water for 100 days at the field capacity

‡ The amount of Cd released to solution

Table 3.4.2 Amount of Cd released from the treated soils by deionized distilled water and 1 M KCl chemical or KCl fertilizer solution at the end of a 15-min reaction period

Soil	Traetment†	DDW		1 M KCl (chemical)		1 M KCl (fertilizer)		pH		Cd_r‡	
		pH	Cd_r	pH	Cd_r	pH	Cd_r	$LSD_{0.05}$	$LSD_{0.01}$	$LSD_{0.05}$	$LSD_{0.01}$
			mg kg^{-1} soil		mg kg^{-1} soil		mg kg^{-1} soil				
Egerton	Idaho MAP‡‡-fertilizer	5.43	0.14	5.77	2.01	5.33	1.88	0.06	0.09	0.08	0.15
	MAP chemical + $Cd(ClO_4)_2$	5.44	0.24	5.91	4.80	5.82	4.56	0.04	0.08	0.07	0.14
Naivasha	Idaho MAP-fertilizer	5.04	0.13	5.52	1.27	5.64	1.15	0.04	0.07	0.08	0.16
	MAP chemical + $Cd(ClO_4)_2$	5.35	0.23	6.70	2.91	5.70	2.80	0.05	0.09	0.07	0.14
Soy	Idaho MAP-fertilizer	5.45	0.13	5.11	2.11	4.80	1.95	0.06	0.10	0.06	0.12
	MAP chemical + $Cd(ClO_4)_2$	5.86	0.23	5.74	4.37	5.24	4.18	0.04	0.08	0.09	0.17
$LSD_{0.05}$		0.04	0.02	0.05	0.15	0.05	0.07				
$LSD_{0.01}$		0.07	0.03	0.08	0.23	0.09	0.11				

† After incubation with the Idaho MAP-fertilizer or MAP chemical plus $Cd(ClO_4)_2$ for 100 days at the field capacity

‡ Cd_r is the amount of Cd released to solution

‡‡ Monoammonium phosphate

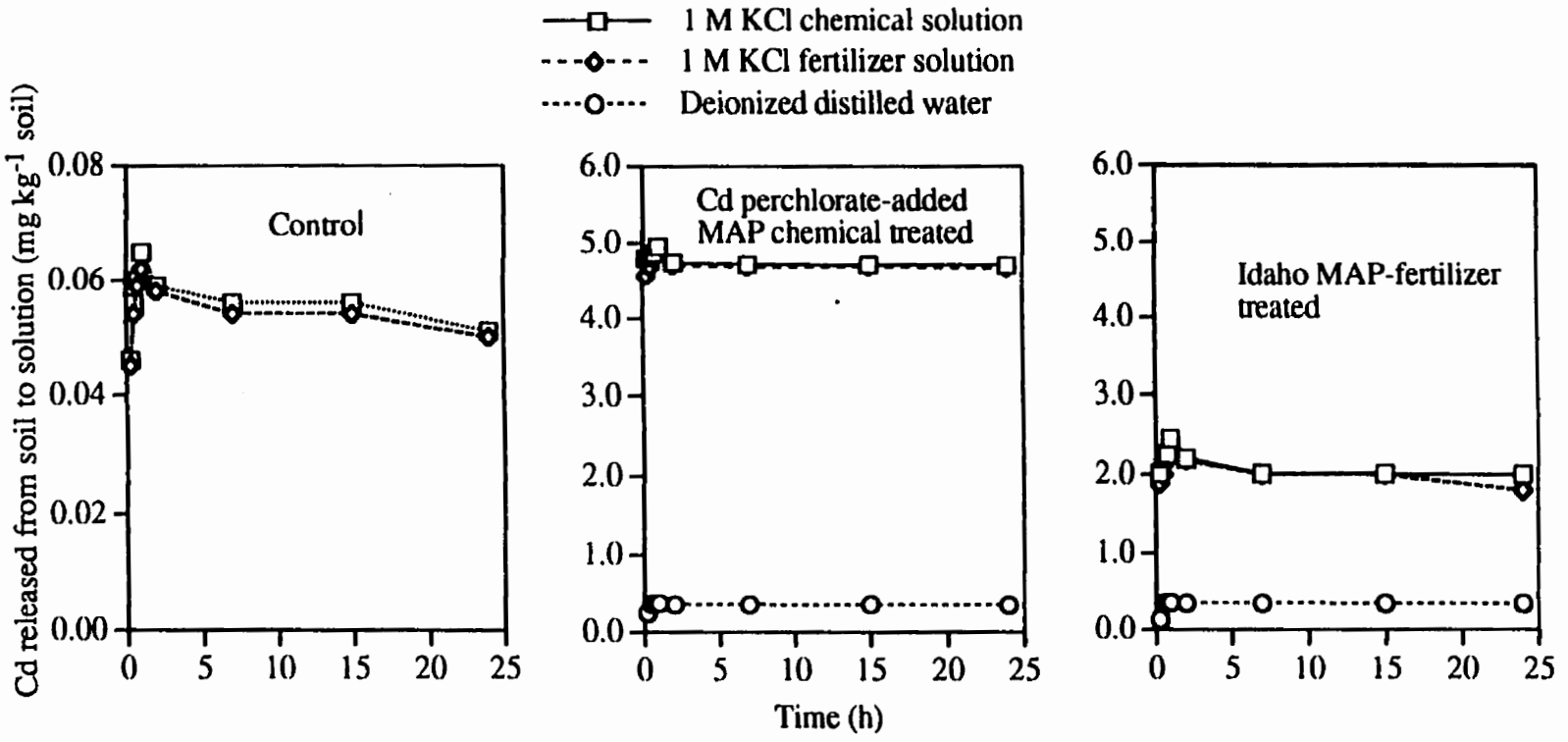

Figure 3.4.1 Changes in the amounts of Cd released by 1 M KCl chemical or 1 M KCl fertilizer solution during the 0.25 to 24 h-reaction period from the control Egerton soil and the Egerton soil treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent. The Cd released from control soils by deionized distilled water was not detectable.

The amount of Cd released by deionized distilled water from the treated soils was much lower compared with the amount of Cd released by KCl chemical or KCl fertilizer from the soils of the same treatment (Figure 3.4.1). The data presented is for the Egerton soil since the other soils followed the same trend. The release of Cd to solution is largely attributed to the formation of Cd-chloride complexes (Hahne and Kroontje, 1973) which enhances the release of Cd from the soils. It has been suggested that Cd^{2+} forms complexes with Cl^- in soil solution (Lindsay, 1979). The formation of stable Cd-chloride complexes (Hahne and Kroontje, 1973) may decrease the sorption of Cd on exchange sites in soil. The formation of these complexes may be responsible for increased solubility and bioavailability of Cd in soils treated with KCl fertilizers, since McLaughlin et al. (1997) recently reported that in saline conditions, Cd-chloride complexes are the dominant Cd species. Bingham et al. (1983) reported that Cd uptake by Swiss chard was considerably enhanced by chloride salts. At high chloride concentrations, the formation of negatively charged complexes accounts for the solubilization of soil Cd. In the present study, the ionic strength of the system was not controlled, hence the release of Cd from the soils may also be attributed to the effect of ionic strength. Naidu et al. (1994a) reported that Cd sorption at the neutral field pH decreased with an increase in the ionic strength of the electrolyte solution. It has been indicated that the presence of chloride in soil solution increases the desorption of Cd from the soil by a factor of 10 as compared to NO_3^- of the same ionic strength (Boekhold et al., 1993). Further, Sakurai and Huang (1996) showed that the desorption rate of Cd on the montmorillonite was higher in the presence of M KCl (90%) compared with M KNO_3 (59%). The difference in the desorption rate between KCl and KNO_3 was attributed to the complex ion formation of Cd with the anionic species. The Cd forms stronger complexes with Cl ion than NO_3 ion. In view of the relatively higher stability constant of the Cd-chloride complexes (log $K_{CdCl^+} = 1.98$, log $K_{CdCl_2^o} = 2.50$, log $K_{CdCl_3^-} = 2.60$ and log $K_{CdCl_4^-} = 2.80$) than the Cd-nitrate complexes (log $K_{CdNO_3^+} = 0.50$, log $K_{Cd(NO_3)_2^o} = 0.20$) (Smith

and Martell, 1976; Dean, 1992), KCl would enhance the desorption rate of Cd from the soils through more complexation with chloride than KNO_3. The presence of K^+ ion in the solution can also affect the Cd sorption on the soils. This effect may be attributed to the increased competition between Cd^{2+} ion and K^+ for sorbing sites. The release of Cd from the soils in the presence of KCl can, therefore, be a combined effect of the formation of Cd-chloride complexes, ionic strength, and to some extent the K^+ ion. However, the exchangeable Cd was not detectable in the natural soils. Therefore, the competing effect of K^+ ion should be negligible in the natural soils. Cadmium forms a wide range of complexes with chloride; however, it is not known if these complexes are adsorbed or weakly adsorbed onto soil particles.

The Cd released from the natural soils and the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent during the 0.25 to 1 h reaction period varied with the concentration of the KCl fertilizer and also with the soil type (Figures 3.4.2, 3.4.3 and 3.4.4). The total Cd content (Table 3.1.2), the metal-organic complex-bound Cd and the organic bound Cd (Table 3.1.7) of the natural Soy soil were one order of magnitude lower than the Egerton soil or the Naivasha soil. This explains the observation that more Cd was released from the natural Egerton or the natural Naivasha soil than the natural Soy soil (Figure 3.4.2). In the case of the treated soils, the Cd released by KCl fertilizer was virtually from the Cd introduced to the soils, since the amount of the Cd released per unit weight of soil (Figures 3.4.3 and 3.4.4) was at least one order of magnitude higher than the amount of Cd content of the natural soils (Table 3.1.2). The same trend was observed for the Cd released by KCl chemical solution from the natural soils and the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical solution (Data not shown).

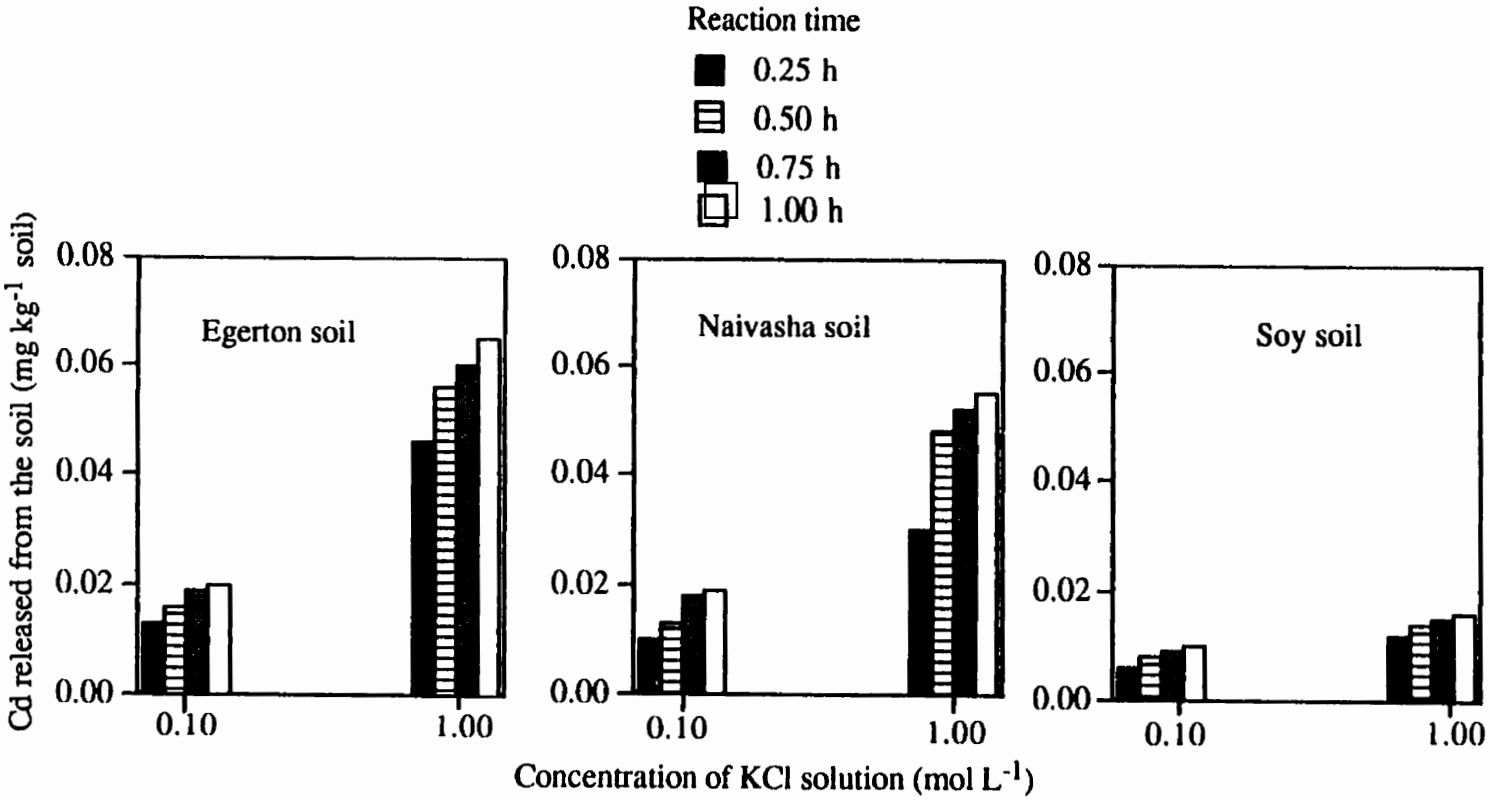

Figure 3.4.2 Amount of Cd released from the control soils by KCl fertilizer solution at various concentrations as a faction of reaction period. The Cd released from the control soils by deionized distilled water or 0.01 M KCl was not detectable

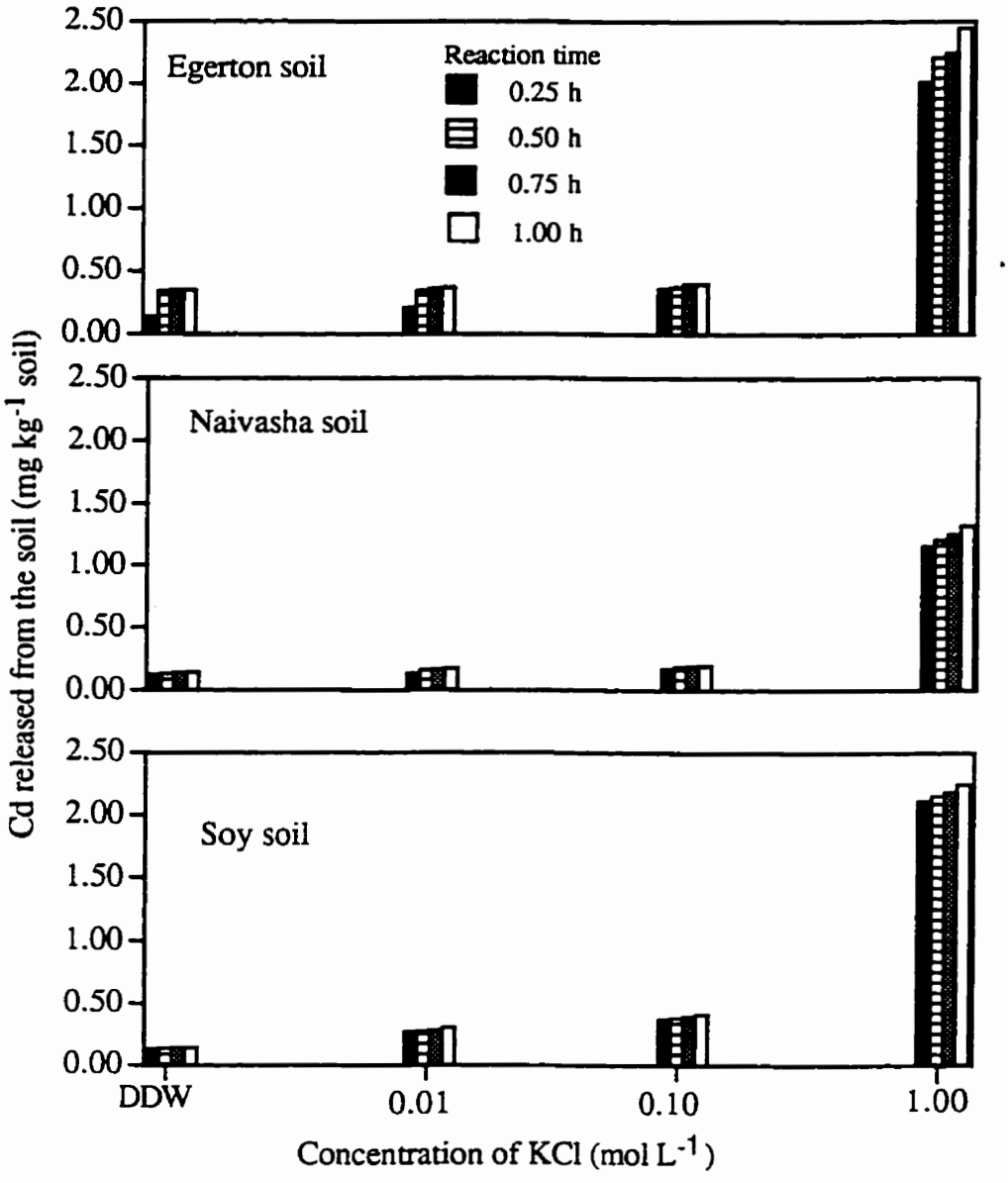

Figure 3.4.3 Amount of Cd released from the Idaho monoammonium phosphate-fertilizer treated soils by deionized distilled water and KCl fertilizer solution at various concentrations as a function of reaction period. DDW stands for deionized distilled water.

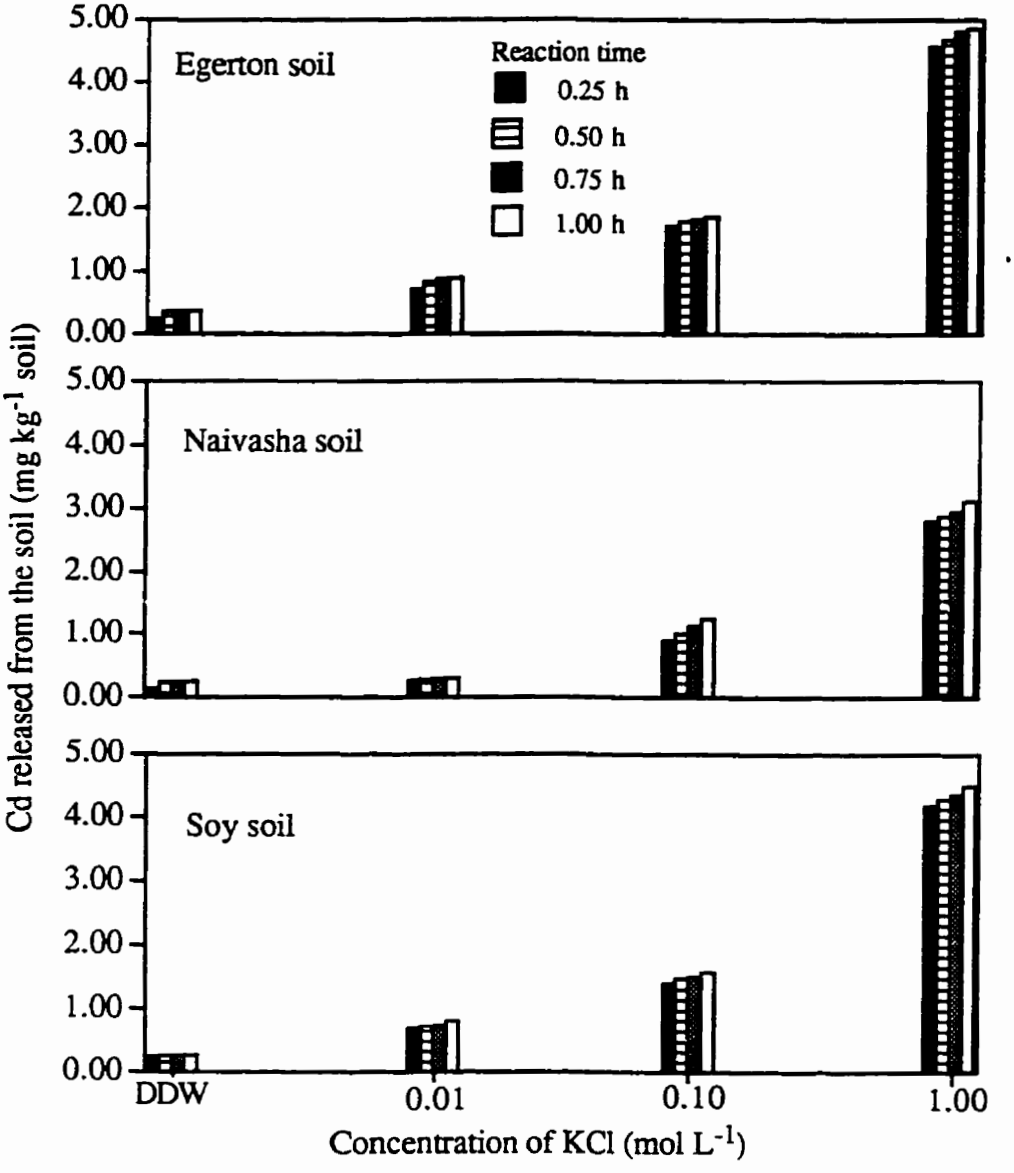

Figure 3.4.4 Amount of Cd released from the soils treated with Cd perchlorate-added monoammnium phosphate chemical reagent by deionized distilled water and KCl fertilizer solution at various concentrations as a function of reaction period. DDW stands for deionized distilled water.

3.4.3.2 Kinetics of cadmium release

The kinetic equations which were used to fit the data on Cd remaining in the sample (Cd_t) or Cd released to solution (Cd_r) versus the reaction time (t) according to Sparks (1989) were presented in Table 3.3.4, Section 3.3. The basis for the selection of the best fit of a kinetic model to calculate the rate of Cd release from the soils was described in Section 3.3.3.2. Overall, the parabolic diffusion equation was found to describe the Cd release from the soils the best, as evidenced from the R^2 and p values presented in Tables 3.4.3 and 3.4.4. The parabolic diffusion equation was, therefore, used to describe the rate of Cd release from the soils during the short-reaction period of 0.25 to 1 h.

The overall diffusion coefficients of Cd release from the soils in the 1.0 M KCl chemical or 1.0 M KCl-fertilizer (muriate of potash) solutions were calculated from the parabolic diffusion equation. The data obtained are presented in Tables 3.4.5 and 3.4.6. The overall diffusion coefficient is taken as a measure of the rate of Cd released from the soils. The overall diffusion coefficients of the KCl-induced Cd release varied with the soils (Table 3.4.5). The rates of Cd release from the natural soils by 1.0 M KCl chemical or fertilizer as indicated by the overall diffusion coefficients (Table 3.4.5) were higher for the Naivasha and Egerton soils compared to the Soy soil. Further, the Cd content (Table 3.1.2), the metal-organic complex bound-Cd and the organic bound-Cd (Table 3.1.7) of the Naivasha and Egerton soils were much higher than the Soy soil. The same trend was observed in the case of LMWOAs (Table 3.3.8). The rates of Cd released from the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent by the KCl chemical or KCl fertilizer were much higher compared to those of Cd released from the same treatments by deionized distilled water, indicating that KCl induced enhancement of the rate of Cd released from the soils (Table 3.4.6). Further, the overall diffusion coefficients were much higher for the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent than for the control soils (Tables 3.4.5

and 3.4.6). The values for the overall diffusion coefficients for the Cd released from the natural soils by LMWOAs or the KCl chemical or KCl fertilizer were in the same order of magnitude; however, the concentration of KCl was higher than that of the LMWOAs used in the study (Table 3.3.8 and 3.4.5). The stability constants of the Cd-chloride complexes (log K_{CdCl^+} = 1.98, log $K_{CdCl_2^0}$ = 2.50, log $K_{CdCl_3^-}$ = 2.60 and log $K_{CdCl_4^{2-}}$ = 2.80) (Smith and Martell, 1976; Dean, 1992) are in the similar order of magnitude as that of the Cd-LMWOA complexes (log $K_{Cd\text{-acetate}}$ = 1.50, log $K_{Cd\text{-citrate}}$ = 3.98, log $K_{Cd\text{-malate}}$ = 2.36, log $K_{Cd\text{-oxalate}}$ = 3.89 and log $K_{Cd\text{-succinate}}$ = 2.10) (Sillen and Martell, 1964). This similarity suggests that NH_4Cl could be used as a soil test for Cd availability index. The data also show the effectiveness of LMWOAs commonly found in the soil rhizosphere in releasing the soil Cd to the soil solution. The overall diffusion coefficients of Cd released from the soils treated with the Idaho MAP-fertilizer were lower than those of the soils treated with the Cd perchlorate-added MAP chemical reagent (Table 3.4.6). This trend was not evident in most of the soils studied in the case of LMWOAs (Table 3.3.9). This may be due to the effectiveness of LMWOAs in releasing Cd from the soils as described above. The $Cd(ClO_4)_2$ $6H_2O$ would react with MAP chemical to form Cd phosphate which is more soluble in water than the Cd present in the Idaho MAP-fertilizer (Street et al., 1978; Mortvedt and Osborn, 1982; Perry and Philips, 1995). Cadmium may have reacted with certain impurities present in the fertilizer, hence hindering its release from the soils treated with the Idaho MAP-fertilizer.

3.4.3.3 Adsorption of cadmium by the soils as influenced by potassium chloride

During the 0.25 to 2.0 h-reaction period, the amount of Cd remaining in solution increased with the increasing concentration of KCl as indicated by plotting Cd remaining in solution on the log scale versus the contact time (Figure 3.4.5).

Table 3.4.3 The statistical analysis of the kinetic data of Cd release from the soils by 1 M KCl chemical reagent solution

Soil	Treatment†	Kinetic equations††					
		Zero-order $Cd_t = a - k_1t$		First-order $lnCd_t = a_1 - k_2t$		Parabolic diffusion $Cd_r = a_2 + Dt^{1/2}$	
		R^2	p	R^2	p	R^2	p
Egerton	Control	0.954	2.3×10^{-2}	0.964	1.7×10^{-2}	0.978	1.1×10^{-2}
	Idaho MAP‡-fertilizer	0.601	8.2×10^{-1}	0.602	8.2×10^{-1}	0.884	3.0×10^{-3}
	MAP chemical + $Cd(ClO_4)_2$	0.935	3.3×10^{-2}	0.951	2.5×10^{-2}	0.976	1.2×10^{-2}
Naivasha	Control	0.828	8.9×10^{-2}	0.854	7.5×10^{-2}	0.899	5.2×10^{-2}
	Idaho MAP-fertilizer	0.917	4.1×10^{-2}	0.914	4.1×10^{-2}	0.956	7.5×10^{-3}
	MAP chemical + $Cd(ClO_4)_2$	0.902	4.9×10^{-2}	0.901	5.0×10^{-2}	0.933	8.7×10^{-3}
Soy	Control	0.966	1.7×10^{-2}	0.994	2.8×10^{-3}	0.996	2.0×10^{-3}
	Idaho MAP-fertilizer	0.978	2.6×10^{-2}	0.980	1.6×10^{-2}	0.989	1.0×10^{-2}
	MAP chemical + $Cd(ClO_4)_2$	0.870	6.7×10^{-2}	0.870	6.7×10^{-2}	0.968	1.5×10^{-2}

† After 100-day incubation at the field capacity

†† Cd_t is the amount of Cd remaining in the soil after reaction time t; Cd_r is the amount of Cd released to solution at the end of a reation period t; a, a_1 and a_2 are constants in the respective equations; k_1 and k_2 are rate constants and D is overall diffusion coefficient

‡ Monoammonium phosphate

Table 3.4.4 The statistical analysis of the kinetic data of Cd release from the soils by 1 M KCl fertilizer solution

Soil	Treatment†	Kinetic Equation††					
		Zero-order $Cd_t = a - k_1 t$		First-order $\ln Cd_t = a_1 - k_2 t$		Parabolic diffusion $Cd_r = a_2 + Dt^{1/2}$	
		R^2	p	R^2	p	R^2	p
Egerton	Control	0.524	2.7×10^{-1}	0.568	2.4×10^{-1}	0.982	8.4×10^{-3}
	Idaho MAP‡-fertilizer	0.984	7.9×10^{-3}	0.982	8.2×10^{-3}	0.985	7.7×10^{-3}
	MAP chemical + $Cd(ClO_4)_2$	0.970	1.5×10^{-2}	0.966	1.7×10^{-2}	0.990	4.6×10^{-3}
Naivasha	Control	0.828	8.9×10^{-2}	0.854	7.5×10^{-2}	0.899	5.2×10^{-2}
	Idaho MAP-fertilizer	0.992	3.8×10^{-3}	0.990	4.0×10^{-3}	0.994	3.7×10^{-3}
	MAP chemical + $Cd(ClO_4)_2$	0.713	1.5×10^{-1}	0.715	1.5×10^{-1}	0.823	2.1×10^{-2}
Soy	Control	0.966	1.7×10^{-2}	0.994	2.8×10^{-3}	0.996	2.0×10^{-3}
	Idaho MAP-fertilizer	0.940	3.0×10^{-2}	0.940	3.0×10^{-2}	0.975	1.2×10^{-2}
	MAP chemical + $Cd(ClO_4)_2$	0.972	1.2×10^{-2}	0.974	1.1×10^{-2}	0.988	5.8×10^{-3}

† After 100-day incubation at the field capacity

†† Cd_t is Cd remaining in the soil after reaction period t; Cd_r is the amount of Cd released to solution at the end of a reaction period t; a, a_1 and a_2 are constants of respective equations; k_1 and k_2 are rate constants and D is overall diffusion coefficient

‡ Monoammonium phosphate

Table 3.4.5 Overall diffusion coefficients of the potassium chloride-induced Cd released from the control soils

Soil†	Overall diffusion coefficients ($mg\ kg^{-1}h^{-0.5}$)				
	DDW‡	1 M KCl (chemical)	1 M KCl (fertilizer)	$LSD_{0.05}$	$LSD_{0.01}$
Egerton	Nd§	0.040	0.030	0.007	0.017
Naivasha	Nd	0.050	0.050	0.006	0.014
Soy	Nd	0.010	0.010	0.003	0.007
$LSD_{0.05}$		0.010	0.010		
$LSD_{0.01}$		0.020	0.020		

† After incubation with deionized distilled water for 100 days at the field capacity

‡ Deionized distilled water

§ Not detectable

Table 3.4.6 Overall diffusion coefficients of the potassium chloride-induced Cd released from the treated soils

Soil	Treatment†	Overall diffusion coefficients ($mg\ kg^{-1}h^{-0.5}$)				
		DDW†† (chemical)	1 M KCl	1 M KCl (fertilizer)	$LSD_{0.05}$	$LSD_{0.01}$
Egerton	Idaho MAP‡-fertilizer	0.03	0.61	0.60	0.01	0.02
	MAP chemical + $Cd(ClO_4)_2$	0.05	1.29	1.23	0.03	0.06
Naivasha	Idaho MAP-fertilizer	0.02	0.36	0.33	0.02	0.03
	MAP chemical + $Cd(ClO_4)_2$	0.04	1.94	1.89	0.04	0.07
Soy	Idaho MAP-fertilizer	0.02	0.25	0.22	0.02	0.03
	MAP chemical + $Cd(ClO_4)_2$	0.06	0.60	0.59	0.02	0.03
$LSD_{0.05}$		0.01	0.06	0.07		
$LSD_{0.01}$		0.02	0.09	0.10		

† After 100-day incubation with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent at the field capacity

†† Deionized distilled water

‡ Monoammonium phosphate

Cadmium is rapidly adsorbed onto the soil in the absence of KCl. The data indicated that in the presence of KCl, Cd adsorption on the soils was reduced. The adsorption of Cd by the soils varied with the KCl concentration (Figure 3.4.5).

The combined effect of K^+ ions competing for adsorption sites, chloride complexation and the ionic strength of the solution (Boekhold et al., 1993) would reduce Cd adsorption by the soils. If the Cd-chloride complex species cannot be adsorbed or are only weakly adsorbed by soil, then they can move to the soil root-interface by diffusion and mass flow processes. The rate of ion species absorption by plants has been reported to depend upon its concentration in the nutrient medium (Mengel and Kirkby, 1987). At low concentrations, it has been indicated that diffusion is the major process for the ion movement in soil solution (Barber, 1984; Van Rees et al., 1990). In soil solutions, Cd can be present at very low concentrations ($< 10^{-7}$ M) (Hirsch and Banin, 1990), indicating that diffusion would be a major process for Cd movement in soil solution. However, at the fertilizer granule-soil interface, the Cd concentration can be as high as 2.8×10^{-3} M (Appendix 6.1). Mass flow might play a significant role in the movement of Cd in soil solution at such high Cd concentrations. The results indicate that the application of potash (KCl) fertilizer to agricultural soils would reduce the adsorption of Cd by soils and enhance the release of the Cd accumulated in soils. The use of KCl fertilizer would, thus, increase the mobility of Cd in soil solution.

3.4.4 Summary and Conclusions

The amounts of Cd released from the natural soils or the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent by KCl chemical or KCl fertilizer solution increased initially up to a reaction period of 1 h and then decreased slowly and tended to reach a plateau with time. The decrease of Cd concentration with time is in part due to readsorption of released Cd on soil particles. The Cd released from the soils by KCl may be attributed largely to the formation of Cd-

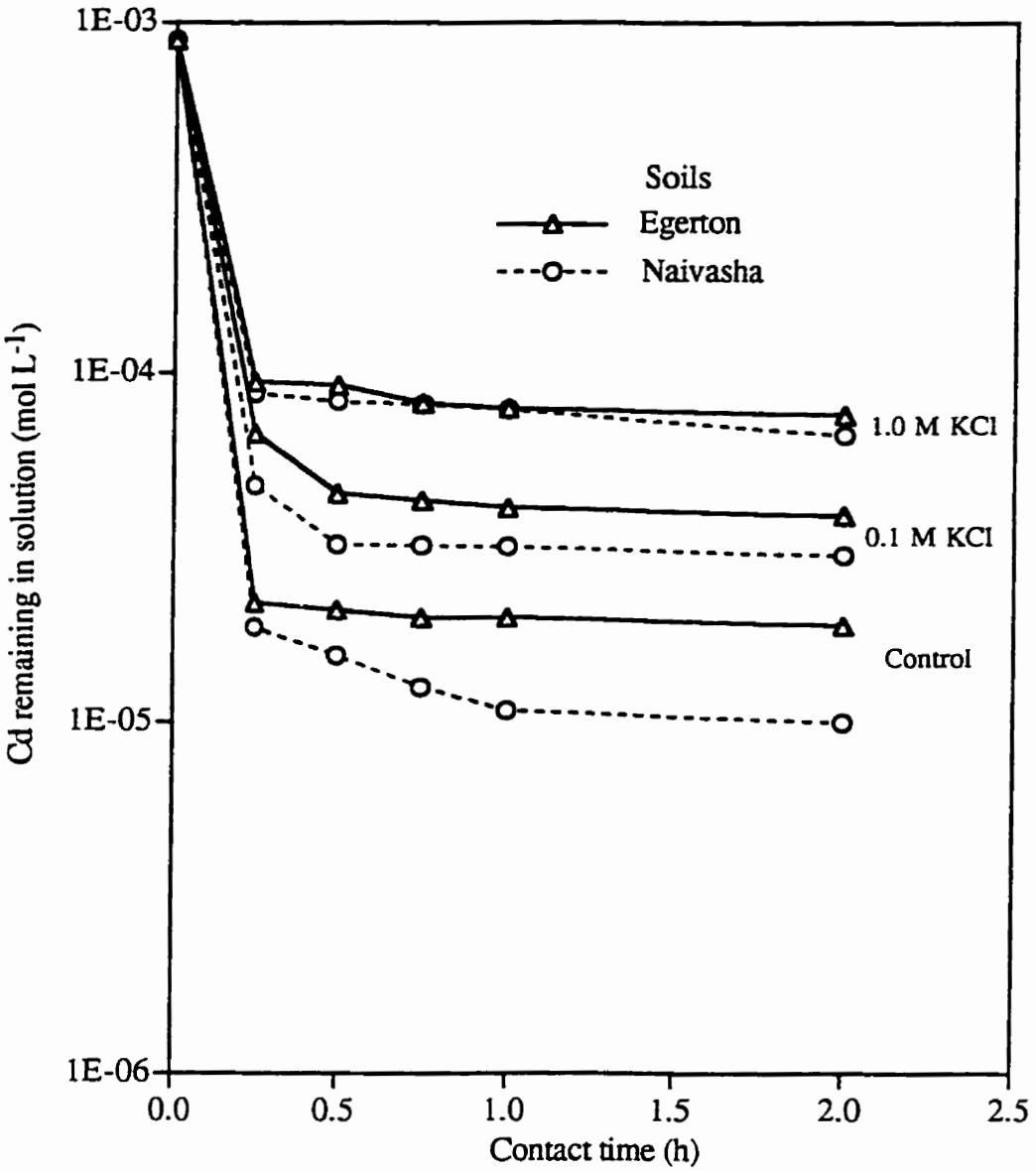

Figure 3.4.5 The influence of KCl concentration on the Cd remaining in solution in the soil-$Cd(ClO_4)_2$ suspension system during the 0.25 to 2 h-reaction period.
Control treatment was deionized distilled water.
The initial Cd concentration at time = 0 was 8.89×10^{-4} M

chloride complexes. Hahne and Kroontje (1973) reported that chloride forms stable complexes with Cd^{2+}. This apparently leads to the increased release of Cd from the soils. Further, since the total Cd concentration in soil solution can be influenced by ionic strength (Boekhold et al., 1993) and other competing ions, e.g. K^+, the Cd released from the soils by KCl may be attributed to the combined effect of all these processes. No detectable amounts of Cd were released from the natural soils by deionized distilled water; however, appreciable amounts of Cd were released from the treated soils by deionized distilled water. The amounts of Cd released from the natural soils during the 15-min reaction period by 1 M KCl fertilizer solution varied with the soil type and was in the following order: Egerton (0.05 mg kg^{-1} soil) > Naivasha (0.03 mg kg^{-1} soil) > Soy (0.01 mg kg^{-1} soil). The same trend was observed when the soils were reacted with KCl chemical solution. Increasing the concentrations of KCl chemical or KCl fertilizer increased the amounts of Cd released during the 0.25 to 1 h reaction period. This would imply that at the fertilizer granule-soil interface where the concentration of Cl^- is expected to be high, more Cd would be solubilized compared to the bulk soil.

The short-term kinetics of Cd release from the soils by 1.0 M KCl chemical or 1.0 M KCl fertilizer solution can be described by the parabolic diffusion equation. The overall diffusion coefficient values of Cd released from the natural soils and the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent varied with the soil and the form of Cd introduced to soils. In the case of the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent, the rates of Cd release by 1.0 M KCl chemical or 1.0 M KCl fertilizer solution were much higher compared to those for deionized distilled water, indicating that KCl substantially enhanced the rate of Cd released from the soils. Further, compared with the natural soils, the rate of Cd released from the soils treated with the Idaho MAP-fertilizer by 1 M KCl was one order of magnitude higher. The application of KCl fertilizers to agricultural fields would reduce the adsorption of Cd by soils and enhance the release of the Cd accumulated in

soils to the soil solution and its uptake by plants. The impact of KCl fertilization on the mobility of Cd and its subsequent food chain contamination, thus, merits attention.

3.5. The Influence of Monoammonium Phosphate on Cadmium Release from Soils

3.5.1 Background

The chemical characteristics of the soil and the source of phosphate fertilizer determine soil fertilizer reactions, which influence P availability to plants (Brady, 1990 ; Tisdale et al., 1993). When phosphate fertilizers are applied to the soils and are dissolved by soil water, reactions occur among the phosphate, soil constituents, and nonphosphatic fertilizer compounds. As a result, the P in the fertilizers becomes fixed due to adsorption and precipitation. The concentration of P in saturated monoammonium phosphate (MAP) solution is 2.9 M with a pH of 3.5 (Lindsay et al., 1962). The nature of the reactions and reaction intensity of phosphate fertilizers with soil constituents should vary with the distance from the fertilizer granule because of the extent of phosphate concentration and pH. In the immediate vicinity of the fertilizer granule, the pH is quite low. When the concentrated P is released into the surrounding soil, the composition of soil solution is altered and this results in the dissolution of some minerals. The dissolution of phosphate fertilizer granules is fairly rapid in soil, even under conditions of low soil moisture (Sample et al., 1980). It has been reported that large quantities of reactive cations such as Fe^{2+}, Al^{3+}, Mn^{2+}, K^{+}, Ca^{2+} and Mg^{2+} can be released during the dissolution processes (Lindsay et al., 1962). Cations from exchange sites may also be displaced by the cations present in these concentrated solutions. Low and Black (1947) found that treating kaolinite with ammonium phosphate solutions (up to 1.5 M) released significant amounts of Si and Al. Similar evidence about the release of cations by solutions of monoammonium phosphate (MAP) and diammonium phosphate (DAP) has been reported by Lindsay et al. (1962).

The high concentration of phosphate and low pH may cause the dissolution of soil constituents such as Al and Fe oxides, kaolinite, montmorillonite and illite (Haseman et al., 1950; Kittrick and Jackson, 1954, 1955, 1956). According to studies by Zhou and Huang (1995), monoammonium phosphate induces the release of K from soils. The combined effect of phosphate and proton on the alteration of the K-bearing minerals was reported to be the major mechanism of K release from the soils in the $NH_4H_2PO_4$ solution.

Phosphate fertilizers which are added to agricultural soils are also known to form various reaction products in soils (Lindsay et al., 1962; Zhou and Huang, 1995). Phosphate concentration of soil solution is a key factor in determining the nature of the reactions. Numerous phosphates are involved in these soil-fertilizer reactions and have been studied by various researchers (Bouldin et al., 1960; Lehr et al., 1959; Lehr et al., 1967; Lindsay et al., 1962). The formation of reaction products in soils is of primary importance because plants obtain their fertilizer phosphorus from these reaction products (Lindsay et al., 1962).

The presence of both ammonium taranakite [$(NH_4)3Al3H_6(PO_4)8.18H_2O$] and potassium taranakite [$K_3Al_5H_6(PO_4)8.18H_2O$] in agricultural soils as P-fertilizer reaction products with soils has been reported (Lindsay et al., 1962; Taylor et al., 1963; Tamimi et al., 1964; Sarkar et al., 1977; Prabhudesai and Kadrekar, 1984; Zhou and Huang, 1995). Taranakites contain N, P, and K in their structures. The formation of taranakites in soils can result in the transformation of these nutrients into forms that are slowly available. Taylor et al. (1960) investigated taranakites as a source of phosphate for plants. The formation of taranakites in soils plays an important role in the nutrient dynamics, especially in the vicinity of the phosphate fertilizers when applied to acidic soils.

However, little is known about the release of Cd in phosphorus deficient acid soils found in the tropics where large amounts of phosphate fertilizers are applied to correct

phosphorus deficiency. The objective of this study was to investigate the kinetics of phosphate-induced Cd release from selected tropical soils in Kenya and also to identify associated phosphate-reaction products in these soils.

3.5.2 Materials and methods

Three soils, Andisol (Egerton), Inceptisol (Naivasha) and Oxisol (Soy) from Kenya were used in this study. The Egerton soil is derived from the volcanic ash and pyroclastic rocks. The Naivasha soil is derived from lacustrine deposits whereas Soy soil is derived from intermediate igneous rocks (syenites, trachytes and phonolites). The properties of these soils were presented earlier in Table 3.1.2

3.5.2.1 Kinetics of cadmium release from the control and treated soils

The concentration of orthophosphate in a saturated solution of $NH_4H_2PO_4$ fertilizer can be as high as 2.90 M (Lindsay et al. 1962). In order to simulate the effect of orthophosphate on Cd release from the soils in the vicinity of fertilizer granules, 1.00 M $NH_4H_2PO_4$ solution was chosen for the kinetic study.

The natural soil samples and the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent were incubated for 100 days at the filed capacity as described in section 3.2.2.1. One gram of each soil (natural soil, Idaho MAP-fertilizer treated soil or Cd perchlorate-added MAP treated soil), in duplicate, was placed in a polypropylene centrifuge tube and 10.0 mL of 1.00 M $NH_4H_2PO_4$ solution was added. The treated soils were washed with deionized distilled water three times to remove any free salts prior to addition of 1.00 M $NH_4H_2PO_4$ solution. The centrifuge tube containing a soil suspension was placed in a water bath shaker at 25°C, with a shaking speed of 60 cycles min^{-1}. At the end of each reaction period (0.25, 0.5, 0.75, 1.0, 2.0, 7.0, 15.0 and 24.0 h), the suspensions were filtered through a 0.45 μm pore-size

membrane under vacuum. The pH of the suspensions was monitored at the end of each reaction period.

Cadmium in the filtrates was determined using a Perkin Elmer 2280 graphite furnace atomic absorption spectrometer (Norwalk, CT) at 228.8 nm using a pyrolytically-coated tube. The furnace parameters used in the determination were the same as those reported by Krishnamurti et al. (1994). The Cd determined in the filtrates (Cd_r) was the Cd released from the soil during reaction time, t. The Cd remaining in the sample (Cd_t) at different reaction times was the difference between the total Cd present in the soil samples and the Cd released to solution.

In the field condition, the concentration of phosphate should decrease gradually with increasing distance from the phosphate fertilizer zone. In order to investigate the influence of phosphate concentration on Cd release , 0.10 M $NH_4H_2PO_4$ and 0.01 M $NH_4H_2PO_4$ solutions were also used in the study of Cd release from the soils according to the procedure described above.

3.5.2.2 Investigation of phosphate reaction products in the soils

One gram of each soil sample was placed in a 50-mL polypropylene centrifuge tube and 10 mL of 1.0 M $NH_4H_2PO_4$ solution was added. The soil suspensions were allowed to shake for different reaction periods, i.e., 15, 50 and 100 days in a water bath shaker at 25°C, with a shaking speed of 60 cycles min^{-1}. The effect of Cd on the formation of phosphate reaction products was also investigated in the presence of 6.4 x 10^{-3} M $Cd(ClO_4)_2 .6H_2O$ using the same procedure described. The Cd concentration of 6.4 x 10^{-3} M was chosen after trials using a lower Cd concentration in the range of 10^{-4} M. The trials indicated that at 10^{-4} M Cd concentration, the formation of phosphate reaction product was not perturbed. At the end of each reaction period, the soil suspensions were filtered as described above in Section 3.5.2.1 and the reaction products were investigated as described below.

The reacted soil samples were leached with 10 mL of deionized distilled water four times to remove the free salt in the soil samples. Each washed soil sample was air-dried and ground to < 5 μm with an agate mortar and pestle and used for XRD and IR analysis. The ground soil samples were directly mounted on a glass slide by adding a few drops of acetone prior to X-ray diffraction analysis by Rigaku D/MaX-RBX X-ray diffraction instrument (Tokyo, Japan) using monochromatic Fe-K_α radiation generated at 40 kV-130 mA. For IR analysis, 1 mg of soil sample (< 5 μm) was mixed with 250 mg KBr and was then pressed into a pellet. The KBr pellet with the sample was examined with a Perkin-Elmer 983 infrared absorption spectrophotometer (Buckinghamshire, England).

The use of 6.4 x 10^{-3} M $Cd(ClO_4)_2 .6H_2O$ in this study to investigate the effect of Cd on the formation of phosphate reaction products in 10 mL of 1 M $NH_4H_2PO_4$ solution is justified because the concentration of Cd at the immediate fertilizer granule-soil interface should be especially high. The Cd content of Idaho monoammonium phosphate (MAP)-fertilizer is 144 mg kg^{-1} (Krishnamurti et al., 1996). The expected high Cd concentration at the fertilizer-soil interface was shown in the calculation for the incubation study (Appendix 6.1). The calculation showed that 0.0231 g of $Cd(ClO_4)_2 .6H_2O$ was required for 100 g soil to give 62.4 mg of Cd kg^{-1} soil at the Idaho MAP-fertilizer granule-soil contact.

3.5.3 Results and discussions

3.5.3.1 The amount of cadmium released from the soils

The Cd released from the natural Egerton, Naivasha and Soy soils during the 15-min reaction period as influenced by 1.00 M $NH_4H_2PO_4$ solution varied with the soils (Table 3.5.1). The form of Cd added to the soils influenced the amount of Cd released from the soils (Table 3.5.2). Cadmium released from the control soils by deionized distilled water was not detectable.

Soil pH is often regarded as the major factor in controlling the plant uptake of Cd from soils (Chaney and Hornick, 1978). The pH effect on Cd availability in soils is largely ascribed to the large effect of pH on the retention of Cd^{2+} by soil surfaces. The initial pH of 1.00 M $NH_4H_2PO_4$ solution was 4.04. The pH of the soil-$NH_4H_2PO_4$ suspension at the end of a 15-min reaction period was in the order : Naivasha (5.09) > Egerton (4.97) > Soy (4.66) for the control soils. The amounts of Cd released from the soils were not in the same order as the pH of soil-$NH_4H_2PO_4$ suspensions. The soy soil which had the lowest soil-$NH_4H_2PO_4$ suspension pH released the lowest amount of Cd. Hence, pH was not a major factor in influencing the amount of the Cd released from the soils in the system studied. However, in terms of percent of the total soil Cd released, the Soy soil (pH of soil-$NH_4H_2PO_4$ suspension = 4.66) released the highest percent of Cd (Table 3.5.1). But the use of the fraction of Cd released from the soils as affected by pH only indicates how easily Cd can be released from the soil, and the use of absolute amounts of Cd released from the soils (mg Cd kg^{-1} soil) is more meaningful in terms of food chain contamination. The amounts of Cd released from the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent by deionized distilled water were one order of magnitude lower than the amounts of Cd released by 1.00 M $NH_4H_2PO_4$ solution (Table 3.5.2), indicating that phosphate substantially induced Cd release from the soils studied.

The amounts of Cd released during the 0.25 to 1 h reaction period from the soils increased with the concentration of $NH_4H_2PO_4$ solution and also varied with soil type (Figures 3.5.1, 3.5.2 and 3.5.3). The lowest Cd release was observed during the 0.25 to 1 h-reaction period (Figure 3.5.1) in the natural Soy soil which is derived from igneous rocks low in Cd. Due to the low Cd content of the natural Soy soil, the amounts of Cd released by 0.10 M $NH_4H_2PO_4$ and 1.00 M $NH_4H_2PO_4$ solutions were almost the same (Figure 3.5.1). No detectable amounts of Cd release were observed for 0.01 M $NH_4H_2PO_4$ solution for the natural soils. However, appreciable amounts of Cd were

released when 0.01 M $NH_4H_2PO_4$ solution was reacted with the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent (Figures 3.5.2 and 3.5.3). The results showed that the phosphate-induced Cd release increased during the short reaction period of 0.25 to 1 h and then decreased with time and tended to reach plateau in both the natural soils and the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent (Figure 3.5.4). The decrease in the Cd released could be due to readsorption of released Cd onto the surface of soil particles and/or formation of insoluble reaction products in solution.

Table 3.5.1 Amount of Cd released from the control soils at the end of a 15-min reaction period by 1 M $NH_4H_2PO_4$ solution

Soil†	pH‡	Cd released (mg kg^{-1} soil)	% Cd released
Egerton	4.97	0.04	25.4
Naivasha	5.09	0.03	25.2
Soy	4.66	0.01	52.6
$LSD_{0.05}$	0.08	0.01	
$LSD_{0.01}$	0.15	0.02	

† Control soils after 100-day incubation period with deionized distilled water at the field capacity

‡ pH of the soil-$NH_4H_2PO_4$ suspension

Table 3.5.2 Amount of Cd released from the treated soils at the end of a 15-min reaction period by deionized distilled water and $NH_4H_2PO_4$ solution

Soil	Treatment[†]	DDW[††]		1 M $NH_4H_2PO_4$	
		pH	Cd_r[‡]	pH	Cd_r
			mg kg^{-1} soil		mg kg^{-1} soil
Egerton	Idaho MAP[‡‡]-fertilizer	5.43	0.14	4.68	1.30
	MAP chemical + $Cd(ClO_4)_2$	5.44	0.24	4.30	3.60
Naivasha	Idaho MAP-fertilizer	5.04	0.13	4.46	1.10
	MAP chemical + $Cd(ClO_4)_2$	5.35	0.23	4.32	1.40
Soy	Idaho MAP-fertilizer	5.45	0.13	4.60	1.30
	MAP chemical + $Cd(ClO_4)_2$	5.87	0.23	4.23	2.50
$LSD_{0.05}$		0.04	0.02	0.06	0.05
$LSD_{0.01}$		0.07	0.03	0.10	0.09

[†] After an 100-day incubation period with the Idaho MAP-Fertilizer or MAP chemical plus $Cd(ClO_4)_2$ at the field capacity

[††] DDW is deionized distilled water

[‡] Cd_r is the amount of Cd released to solution

[‡‡] Monoammonium phosphate

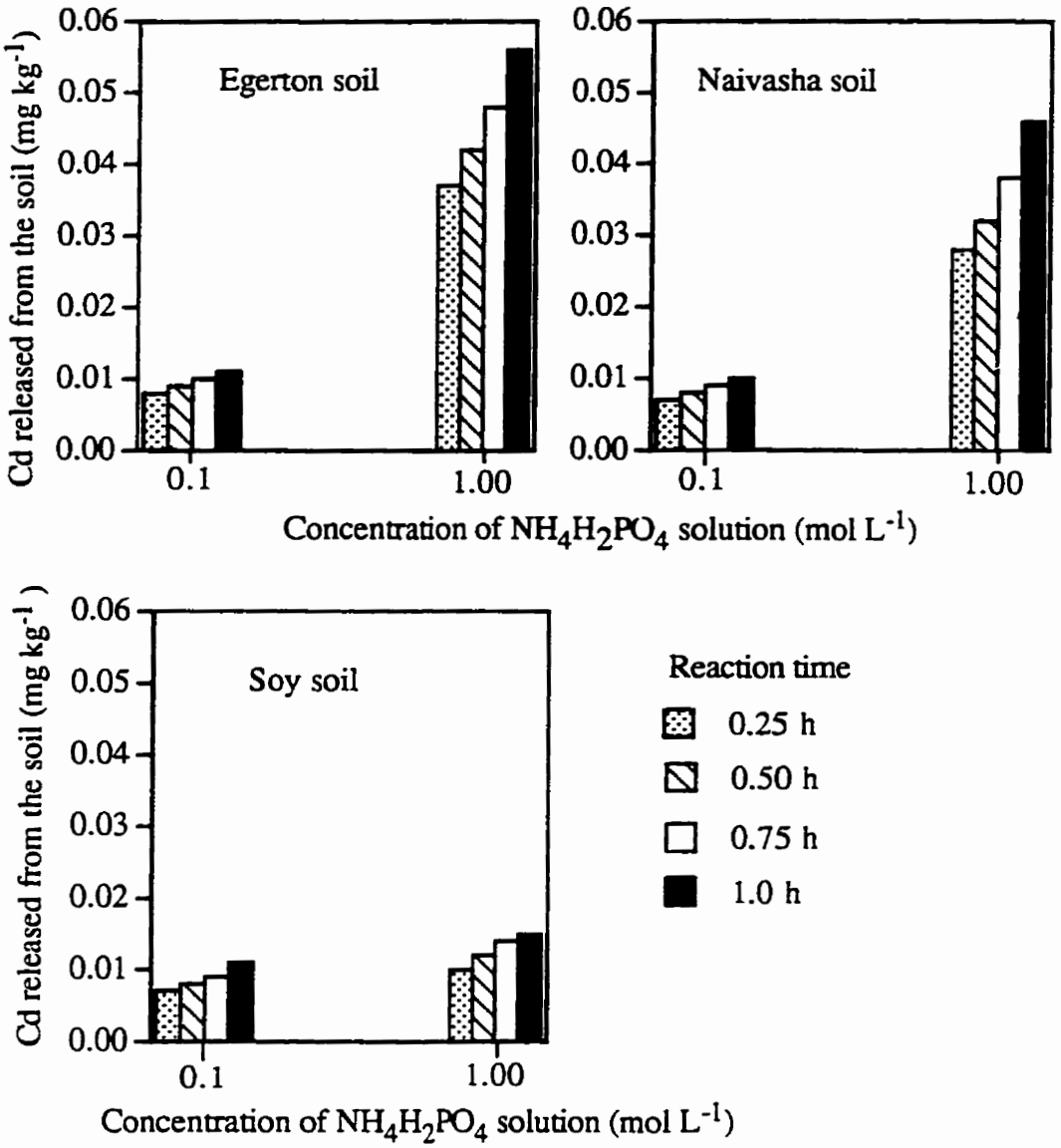

Figure 3.5.1 Amount of Cd released from the control soils by 1 M $NH_4H_2PO_4$ solution at various concentrations as a function of reaction period. Cd released by 0.01M $NH_4H_2PO_4$ was not detectable.

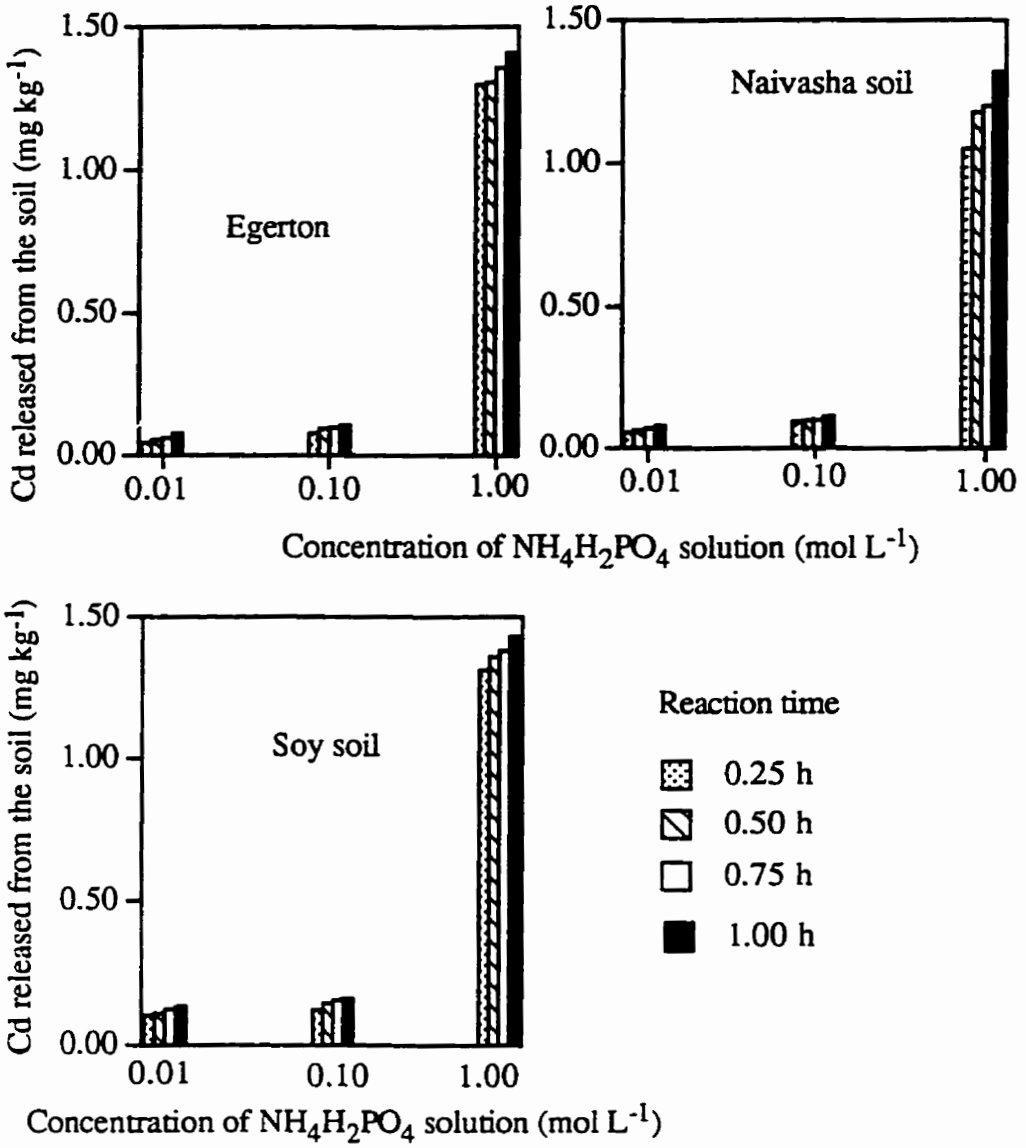

Figure 3.5.2 Amount of Cd released from the Idaho monoammonium phosphate-fertilizer treated soils by $NH_4H_2PO_4$ solution at various concentrations as a function of reaction period

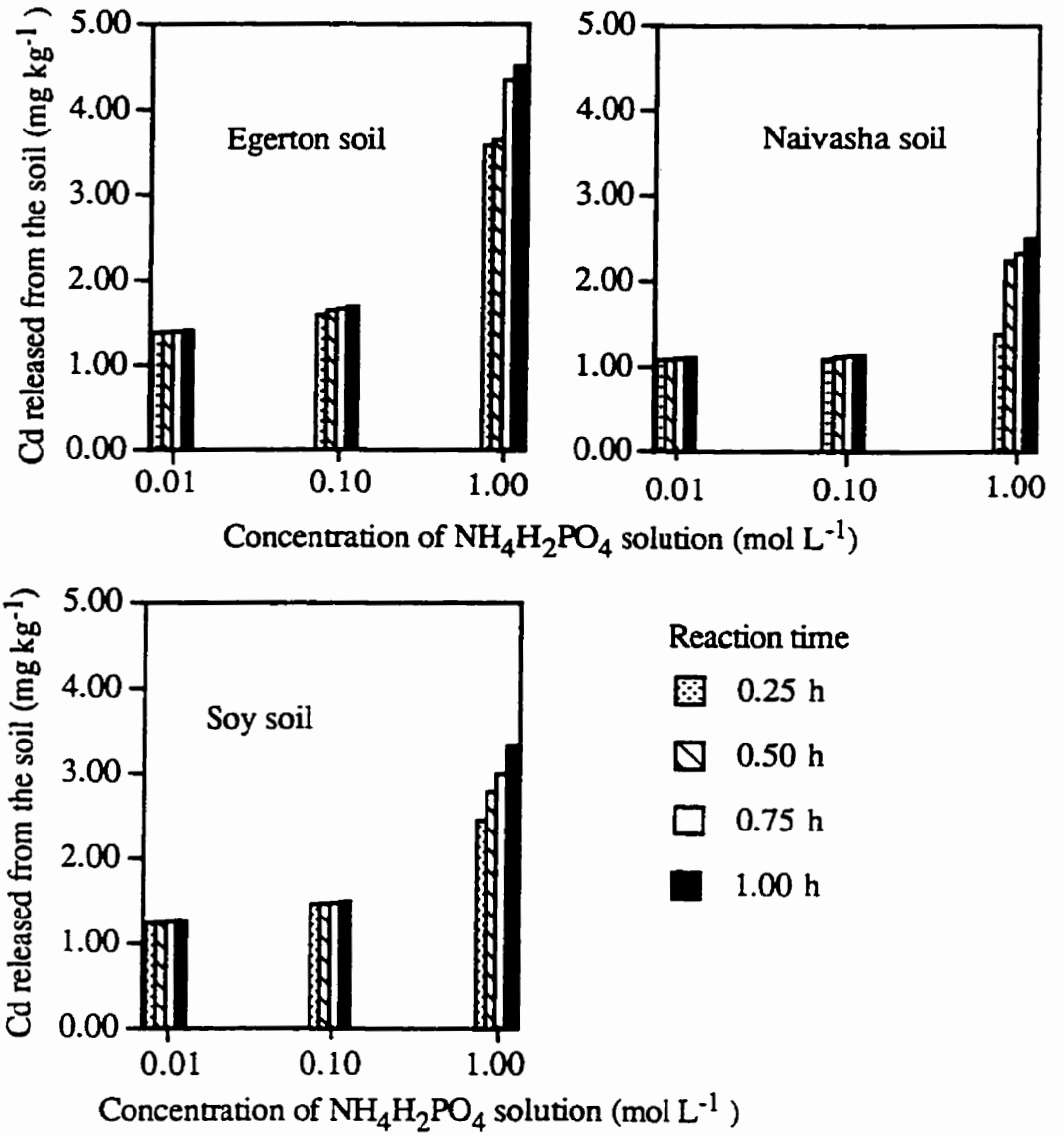

Figure 3.5.3 Amount of Cd released from the soils treated with the Cd perchlorate-added monoammonium phosphate chemical reagent by $NH_4H_2PO_4$ solution at various concentrations as a function of reaction period

In the natural soils, the Cd release (Figure 3.5.4) varied with the Cd content (Table 3.1.2) and the Cd speciation of the soils (Table 3.1.7). For example the Cd content and the metal-organic complex-bound and organic-bound Cd of the surface horizon of the Soy soil were two orders of magnitude lower than those of the other soils studied. However, when Cd was added to the soils, the Naivasha soil released the lowest amount of Cd (Figure 3.5.4). Apparently, compared with the other two soils, the Naivasha soil retained the Cd added more strongly and thus, limited its release. The Mn content of the surface horizon of the Naivasha soil was one order of magnitude higher compared to the Egerton or Soy soil (Table 3.1.2). The oxides of Mn are good adsorbents for heavy metals. The added Cd was apparently adsorbed by the Mn oxides present in the Naivasha soil. This apparently limited the release of Cd from the Naivasha soil (Figure 3.5.4). The other soil components, e.g., organic C, oxides of Al and Fe which can bind Cd in the surface horizon of Naivasha soil were not higher than those of the surface horizons of the Egerton and the Soy soils (Table 3.1.2).

Mortvedt and Osborn (1982) suggested that the chemical form of Cd contained in P-fertilizers, e.g., Idaho MAP-fertilizer, was $Cd(H_2PO_4)_2$, $CdHPO_4$, or a mixture of these salts. In soil solution Cd can precipitate as $Cd_3(PO_4)_2$ ($K_{sp} = 2.5 \times 10^{-33}$) (Dean, 1992). The formation of this sparingly soluble Cd compound in solution could reduce the amount of Cd released to solution with time.

3.5.3.2 Kinetics of cadmium release

The short reaction period of 0.25 to 1 h was used to establish the kinetics of Cd release by 1.00 M $NH_4H_2PO_4$ solution from the soils. Various kinetic models were used to fit the data on Cd remaining in the sample (Cd_t) or Cd released to solution (Cd_r) versus the reaction time (t) (Sparks, 1989). The kinetic models examined in this study were presented in Table 3.3.4, Section 3.3.

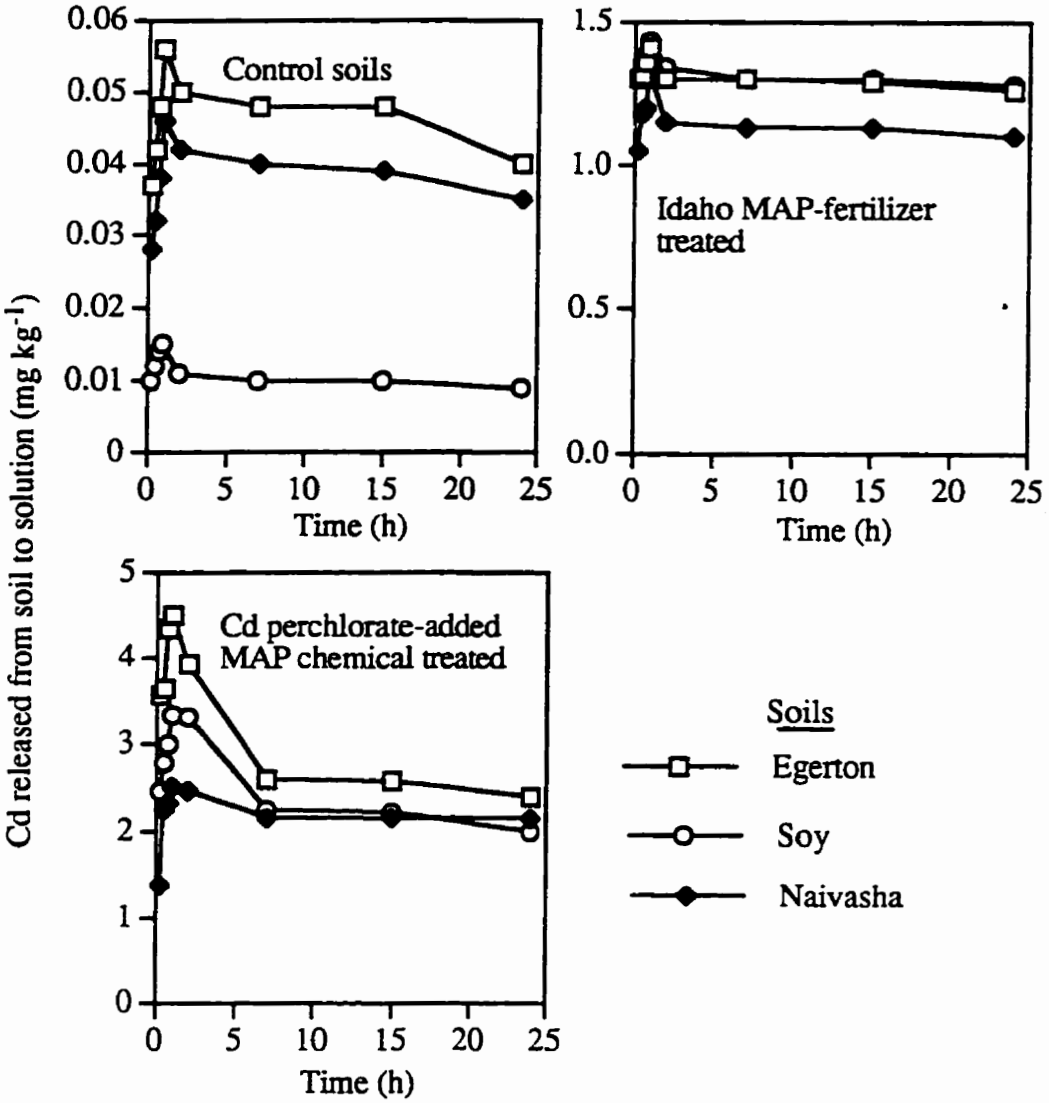

Figure 3.5.4 Changes in the amounts of Cd released by 1 M $NH_4H_2PO_4$ solution during the 0.25 to 24 h reaction period from the control soils and the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added monoammonium phosphate chemical reagent

The reason for using the absolute amounts of Cd released (mg Cd kg^{-1} soil) instead of fractions of Cd released in calculating the rate constants was explained in Section 3.3.3.2. The zero-order and the first-order models were found to generally fit the data better than parabolic diffusion model as evidenced from the R^2 and p values presented in Table 3.5.3. Since the zero-order and the first-order equations fitted the data virtually equally well, the zero-order equation was selected to establish the kinetics of Cd release during the short-reaction period of 0.25 to 1h reaction period.

The rate constants of Cd release from the soils in the 1.00 M $NH_4H_2PO_4$ solution were calculated from the zero-order kinetic equation. The data obtained are shown in Tables 3.5.4. and 3.5.5. The rate of Cd release from the soils varied with the soils and also with the form of Cd introduced to soils (Table 3.5.5). The amount of Cd released based on the rate of Cd released from the soils during the 0.25 to 1 h-reaction period (Tables 3.5.4 and 3.5.5) was lower, compared to the amount of Cd detected in the solution at the end of 1 h-reaction period (Figure 3.5.4). This indicates that the rate of Cd release in the soil system before the 0.25 h was extremely fast. This accounts for the differences between the amount of Cd released after 1 h and the amount of the Cd released based on the rate constant calculated from the zero-order equation. As had been observed in the rates of Cd released from the soils by LMWOAs (Table 3.3.9) and KCl (Table 3.4.6), the Cd introduced in the form of the Cd perchlorate had the highest release rate from all the soils. This could be attributed to the high solubility of Cd perchlorate compared to the Cd in Idaho MAP-fertilizer. Also, Cd could have reacted with some impurities present in the fertilizer, hence interfering with its release from the soils treated with the Idaho MAP-fertilizer. The rate of phosphate-induced Cd release from the control soils followed the order: Egerton (0.03 mg kg^{-1} h^{-1}) > Naivasha (0.02 mg kg^{-1} h^{-1}) > Soy (0.01 mg kg^{-1} h^{-1}) while for the soils treated with the Idaho MAP-fertilizer the order was: Naivasha (0.33 mg kg^{-1} h^{-1}) > Egerton (0.15 mg kg^{-1} h^{-1}) = Soy (0.15 mg kg^{-1} h^{-1}) and for the soils treated with the Cd-added MAP chemical reagent, the order was:

Table 3.5.3. The statistical analysis of the kinetic data of Cd release from the soils by 1 M $NH_4H_2PO_4$

Soil	Treatment†	Kinetic Equation‡					
		Zero-order $Cd_t = a - kt$		First-order $\ln Cd_t = a_1 - k_1 t$		Parabolic diffusion $Cd_r = a_2 + Dt^{1/2}$	
		R^2	p	R^2	p	R^2	p
Egerton	Control	0.988	6.0×10^{-3}	0.982	9.0×10^{-3}	0.773	1.2×10^{-1}
	Idaho MAP§-fertilizer	0.937	3.2×10^{-2}	0.935	3.2×10^{-2}	0.878	6.3×10^{-2}
	MAP chemical+ $Cd(ClO_4)_2$	0.848	7.8×10^{-2}	0.848	7.8×10^{-2}	0.643	1.9×10^{-1}
Naivasha	Control	0.978	1.1×10^{-2}	0.968	1.6×10^{-2}	0.734	1.4×10^{-1}
	Idaho MAP-fertilizer	0.939	3.1×10^{-2}	0.937	3.1×10^{-2}	0.939	3.1×10^{-2}
	MAP chemical + $Cd(ClO_4)_2$	0.793	1.1×10^{-1}	0.793	1.1×10^{-1}	0.865	6.9×10^{-2}
Soy	Control	0.978	1.0×10^{-2}	0.994	3.0×10^{-3}	0.903	5.0×10^{-2}
	Idaho MAP-fertilizer	0.974	1.2×10^{-2}	0.974	1.2×10^{-2}	0.968	1.6×10^{-2}
	MAP chemical + $Cd(ClO_4)_2$	0.992	4.0×10^{-3}	0.992	4.0×10^{-3}	0.863	7.0×10^{-2}

† 100 days incubation at the field capacity

‡ Cd_t is the amount of Cd remaining in the soil after reaction time t; Cd_r is the amount of Cd released to solution at the end of reaction period t; a, a_1 and a_2 are constants in the respective equations; k and k_1 are rate constants and D is the overall diffusion coefficient.

§ Monoammonium phosphate

Table 3.5.4 Rate constants for the Cd release from the control soils by 1 M $NH_4H_2PO_4$ solution during the 0.25 to 1 h-reaction period

Soil†	Rate constant (mg kg^{-1} h^{-1})
Egerton	0.03
Naivasha	0.02
Soy	0.01
$LSD_{0.05}$	0.01
$LSD_{0.01}$	0.02

† After incubation with deionized distilled water for 100 days at the field capacity

Table 3.5.5 Rate constants for the Cd release from the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent by deionized distilled water and 1 M $NH_4H_2PO_4$ solution during the 0.25 to 1 h-reaction period

Soil	Treatment[†]	Rate constants (mg kg^{-1} h^{-1})	
		DDW[††]	$NH_4H_2PO_4$
Egerton	Idaho MAP[‡‡]-fertilizer	0.02	0.15
	MAP chemical + $Cd(ClO_4)_2$	0.03	1.24
Naivasha	Idaho MAP-fertilizer	0.02	0.33
	MAP chemical + $Cd(ClO_4)_2$	0.02	1.37
Soy	Idaho MAP-fertilizer	0.01	0.15
	MAP chemical + $Cd(ClO_4)_2$	0.03	1.12
$LSD_{0.05}$		0.01	0.04
$LSD_{0.01}$		0.02	0.07

[†] After 100-day incubation with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent at the field capacity

[††] Deionized distilled water

[‡‡] Monoammonium phosphate

Naivasha (1.37 mg kg^{-1} h^{-1}) > Egerton (1.24 mg kg^{-1} h^{-1}) > Soy (1.12 mg kg^{-1} h^{-1}). In the case of the treated soils, it was observed that the Naivasha soil had the highest rate of Cd release during the 0.25 to 1h-reaction period compared with the Egerton and the Soy soils (Table 3.5.5); however, the amount of Cd released from the Naivasha soil treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent as a function of time was lower compared to those of the treated Egerton and Soy soils (Figures 3.5.2 and 3.5.3). Apparently the Cd which was retained by the Naivasha soil accounted for the high Cd release rate observed during the 0.25 to 1 h-reaction period (Table 3.5.5). In the natural soils, the rate constant of Cd release by 1.00 M $NH_4H_2PO_4$ (Table 3.5.4) from the Soy soil was lower than that from the Naivasha or Egerton soil. The metal-organic complex-bound Cd and the organic-bound Cd of the surface horizon of the Soy soil were one order of magnitude lower than those of the Naivasha and the Egerton soils (Table 3.1.7). This indicates that more Cd would be released from the Naivasha and Egerton soils than from the Soy soil. The rate constants of Cd release from the treated soils by the deionized distilled water were much lower than those of Cd released by the mono-ammonium phosphate solution (Table 3.5.5), indicating that the application of the Idaho MAP-fertilizer substantially enhanced the rate of Cd released from the soils.

3.5.3.3 Identification of reaction products

Crystalline reaction products were found in the phosphate (1.00 M MAP chemical solution) treated soil samples by X-ray diffraction analysis at the end of each reaction time (15, 50 and 100 days). The main d-spacings of the reaction products were: 15.88, 7.92, 7.49, 7.20 and 5.83 Å in both the Egerton and the Naivasha soils (Figure 3.5.5). The d-spacings compared well with the d-spacings of the standard taranakites (NH_4-taranakite and K-taranakite) synthesized by Taylor and Gurney (1961), Frazier and Taylor, 1965, and Zhou and Huang (1995).

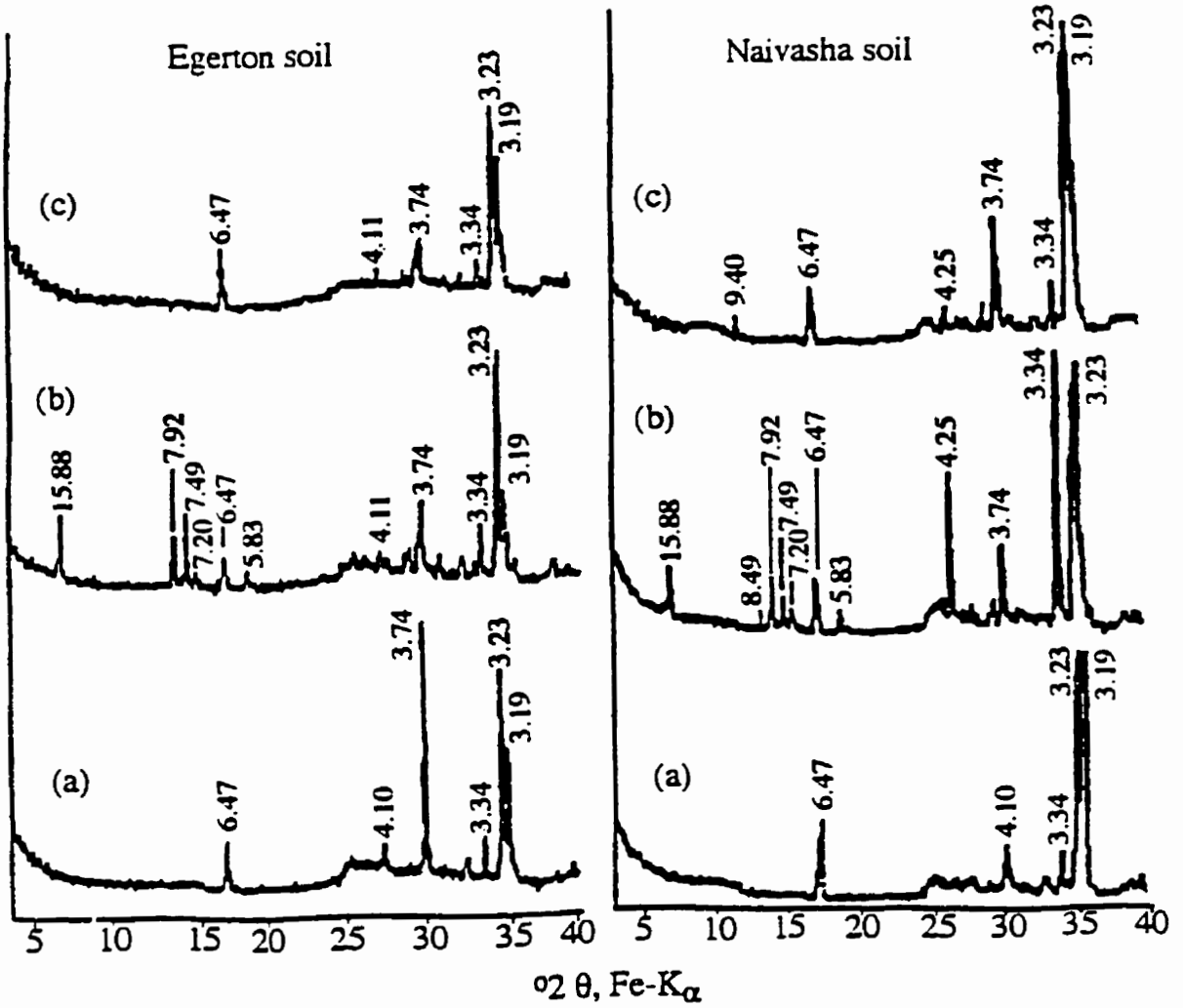

Figure 3.5.5 X-ray diffractograms of the soils treated with 1 M $NH_4H_2PO_4$ both in the presence and absence of 6.4 x 10^{-3} M $Cd(ClO_4)_2$ at 25 °C for 100 d. (a) Control (b) 1 M $NH_4H_2PO_4$ solution and (c) 1 M $NH_4H_2PO_4$ + 6.4 x 10^{-3} M $Cd(ClO_4)_2$. Characteristic d-spacings of NH_4-taranakite are: 15.88, 7.92, 7.49, 7.20 and 5.83 Å.

The standard NH_4-taranakite [$(NH_4)_3Al_5H_6(PO_4)_8.18H_2O$] and K-taranakite [$K_3Al_5H_6(PO_4)_8.18H_2O$] have identical main d-spacings. The peak at 6.47 d-spacing which consistently appeared in the control soils and the treated soils indicates the presence of feldspars (Jackson, 1979). The peaks at d-spacing of 3.19-3.23 Å also indicate the presence of feldspars, e.g., K-feldspars or plagioclase feldspars (Joint Committee on Powder Identification Standards, 1974; Jackson, 1979). The peak at 3.74 Å which was present in the control and the treated soils could also indicate the presence of feldspars (Joint Committee on Powder Diffraction Standards, 1974). It has been reported that the quantities of feldspars in the soils would vary with the nature of the parent material and the stage of weathering (Somasiri et al., 1971). In moderately weathered soils, there are usually considerable quantities of K-feldspars, whereas in strongly weathered soils such as those in the humid tropics, K-feldspars are often present in small amounts (Prabhudesai and Kadrekar, 1984).

In the Egerton soil, the peak at 4.11 Å which appeared even in the control soils, could be goethite. The peaks at 3.34 Å indicate the presence of quartz. In the treated Naivasha soil, the peak at 4.25 Å which did not appear in the control soil could be due to a phosphate reaction product. Prabhudesai and Kadrekar (1984) reported that variscite ($AlPO_4.2H_2O$) can form in soils as a monoammonium phosphate reaction product in soils and has a peak at 4.22 Å.

The peak observed in the X-ray diffractogram of the Naivasha soil at 9.40 Å could arise from a phosphate reaction product. Frazier and Taylor (1965) reported the occurrence of $NH_4AlPO_4OH.{}_2H_2O$ with a d-spacing 9.74 Å. The peak at 8.49 Å observed in the Naivasha soil (Figure 3.5.6) could be a compound of ammonium aluminum phosphate hydrate [$(NH_4)_2AlH(PO_4)_2 . 4HO_2$)] (Frazier and Taylor, 1965; Taylor et al., 1965). After heating at 110 °C, the 8.49 Å peak disappeared (Figure 3.5.6). The formation of ammonium aluminum phosphate compounds in soils when ammonium phosphate fertilizers are applied was reported by Frazier and Taylor (1965). The 8.49 Å

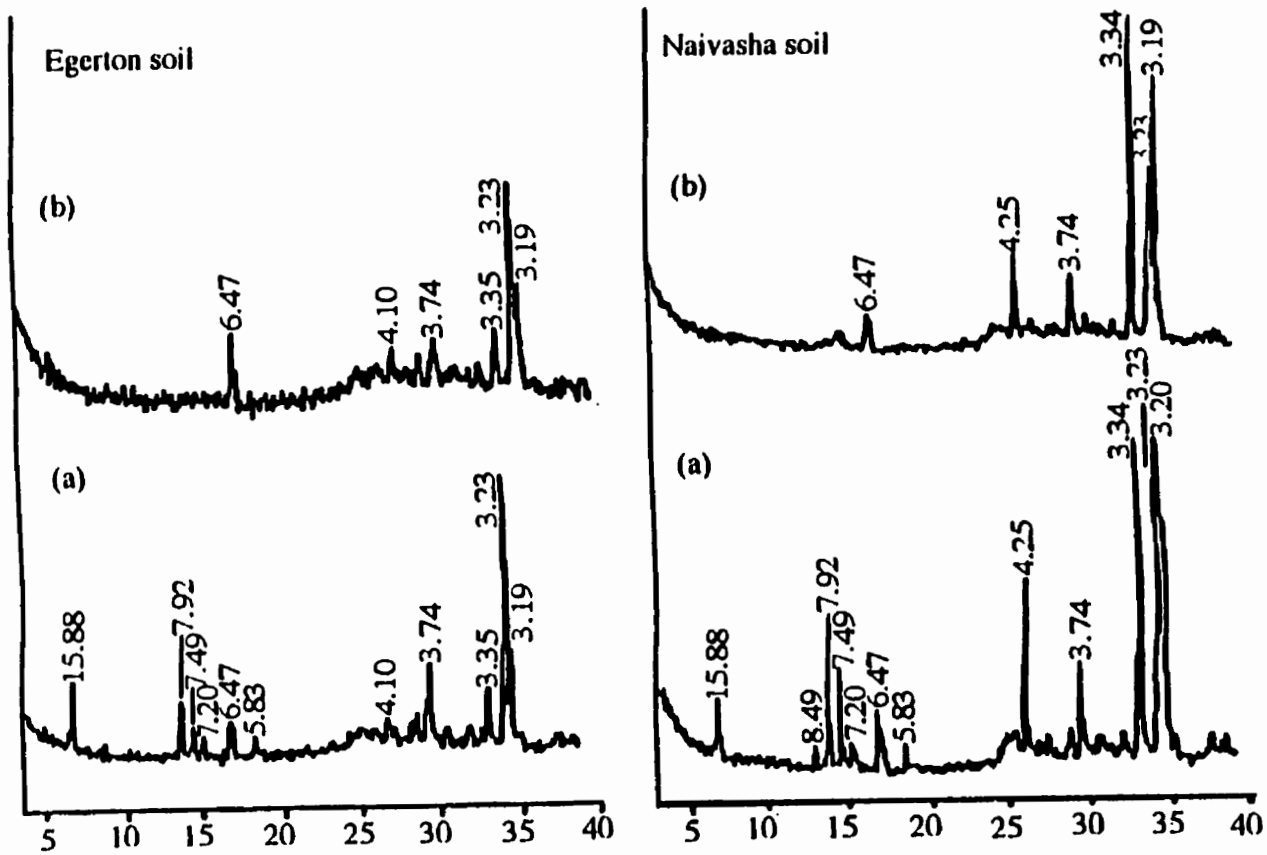

Figure 3.5.6 X-ray diffractograms of NH_4-taranakite formed in the soils treated with 1 M $NH_4H_2PO_4$ solution at 25 °C for 100 d. (a) Before heating and (b) after heating in air at 110 °C for 2h. Characteristic d-spacings of NH_4-taranakite are: 15.88, 7.92, 7.49, 7.20 and 5.83 Å.

peak was not observed in the Egerton soil, which indicates that the formation of phosphate reaction products also varies with the soil type.

When the taranakite formed was heated in air at 110 ^{0}C for 2 h and then examined by XRD, the characteristic d-spacings of taranakites (15.88, 7.92, 7.49, 7.20 and 5.83 Å) disappeared, indicating that the taranakite became XRD-noncrystalline (Figure 3.5.6). Zhou (1995) reported that when heated in air at 110 ^{o}C for 2 h, K-taranakite transforms to new crystalline product whereas NH_4-taranakite transforms to noncrystalline state. The product formed in the present study was therefore identified as NH_4-taranakite. The reacting solution contained 1.00 M NH_4^+ and 1.00 M phosphate, hence if the soils released enough Al^{3+}, NH_4-taranakite would easily be formed. In the control soils (treated only with deionized distilled water) no taranakite was detected at the end of each reaction period. The evidence of release of Cd to solution with time (section 3.5.3.1) indicates that the application of monoammonium phosphate fertilizers to soil should increase the Cd concentration in the soil solution whereas the formation of ammonium taranakite (Figures 3.5.5 and 3.5.6) may lead to the conversion of some of the nitrogen and phosphate in the fertilizer to slowly available forms.

In the presence of 6.4 x 10^{-3} M $Cd(ClO_4)_2$ no taranakite was formed (Figure 3.5.5), indicating that Cd even at 6.4 x 10^{-3} M $Cd(ClO_4)_2$ perturbed the formation of taranakite. The choice of $Cd(ClO_4)_2$ concentration at this order of magnitude was based on the previous calculation for the incubation studies (Appendix 6.1). During the study, a series of Cd concentrations were investigated and a Cd concentration of 6.4 x 10^{-3} M $Cd(ClO_4)_2$ perturbed the formation of taranakite. At Cd concentration of 6.4 x 10^{-4} M, the taranakite formation was not perturbed. Perturbation of taranakite formation by iron has been reported (Zhou, 1995).

To investigate further the nature of the reaction product, infrared analysis was conducted using a Pekin-Elmer 983 infrared absorption spectrophotometer (Buckinghamshire, England) as was described in section 3.5.2.2. The infrared spectra of

the reaction product are shown in Figures 3.5.7 and 3.5.8 for the Egerton and Naivasha soils, respectively. Ammonium ion (NH_4^+) has absorption bands which occur in the region 3350-3050 cm^{-1} (Gadsden, 1975) and may be obscured or confused with the absorptions arising from the presence of water. The absorption bands between 3600 and 2900 and 1639-1626 cm^{-1} (Figures 3.5.7 and 3.5.8) indicate the presence of water and hydroxyl (Frazier and Taylor, 1965; Zhou, 1995). The characteristic absorption band at 3200 cm^{-1} (Figures 3.5.7b and 3.5.8b) was attributed to NH_4-taranakite (Zhou, 1995). The bands less than 1300 cm^{-1} can be attributed to the phosphate (Frazier and Taylor, 1965; Gadsden, 1975; Zhou, 1995). Heating does not affect the bands related to phosphates in the structure of taranakite (Zhou, 1995). The infrared analysis data of the samples before and after heating in air at 110 ^oC for 2 h are presented in Figures 3.5.9 and 3.5.10 for the Egerton and Naivasha soils, respectively. After heating at 110 ^oC for 2 h, the absorption band at 3200 cm^{-1} disappeared (Figure 3.5.9 and 3.5.10), indicating that the ammonium taranakite structure was destroyed (Zhou, 1995). This IR evidence was in accord with the X-ray evidence that NH_4-taranakite was formed in the reaction products.

3.5.4 Summary and conclusions

The release of Cd from the natural soils or soils treated with the Idaho MAP fertilizer or the Cd perchlorate-added MAP chemical reagent by $NH_4H_2PO_4$ solution increased with time for a 1-h reaction period, beyond which the Cd release decreased and then approached plateau. The decrease of the Cd concentration with time is apparently due to readsorption of the released Cd onto the surface of soil particles and/or formation of sparingly soluble reaction products in the solution. The amounts of Cd released from the natural soils by 1 M $NH_4H_2PO_4$ solution during the 15-min reaction period varied with the soil types and generally followed the order: Egerton (0.04 mg kg^{-1} soil) > Naivasha (0.03 mg kg^{-1} soil) > Soy (0.01 mg kg^{-1} soil).

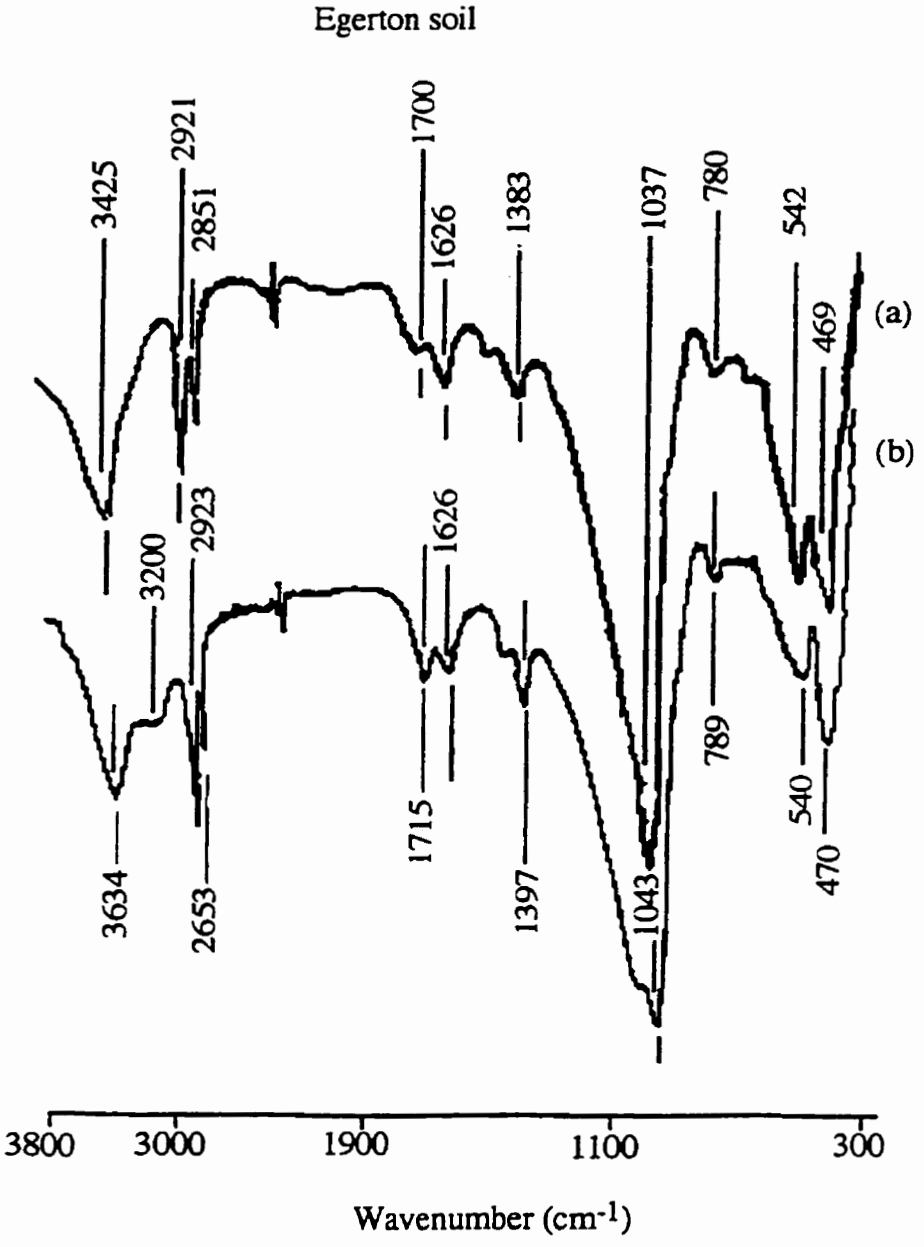

Figure 3.5.7 Infrared spectra of the Egerton soil before and after treatment with 1 M $NH_4H_2PO_4$ for 100 days at 25 °C. (a) control soil and (b) treated soil

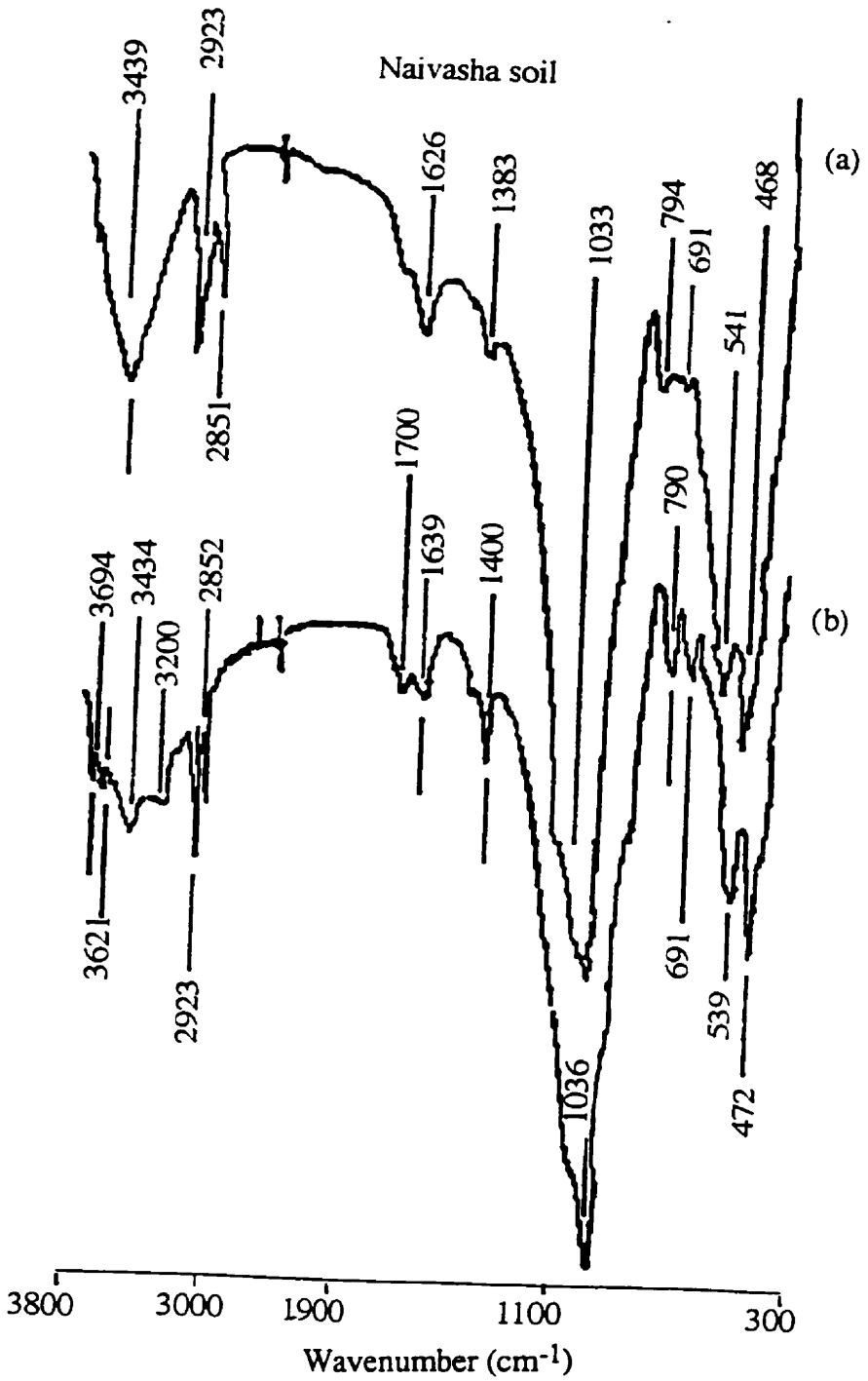

Figure 3.5.8 Infrared spectra of the Naivasha soil before and after treatment with 1 M $NH_4H_2PO_4$ for 100 days at 25 °C. (a) control soil and (b) treated soil

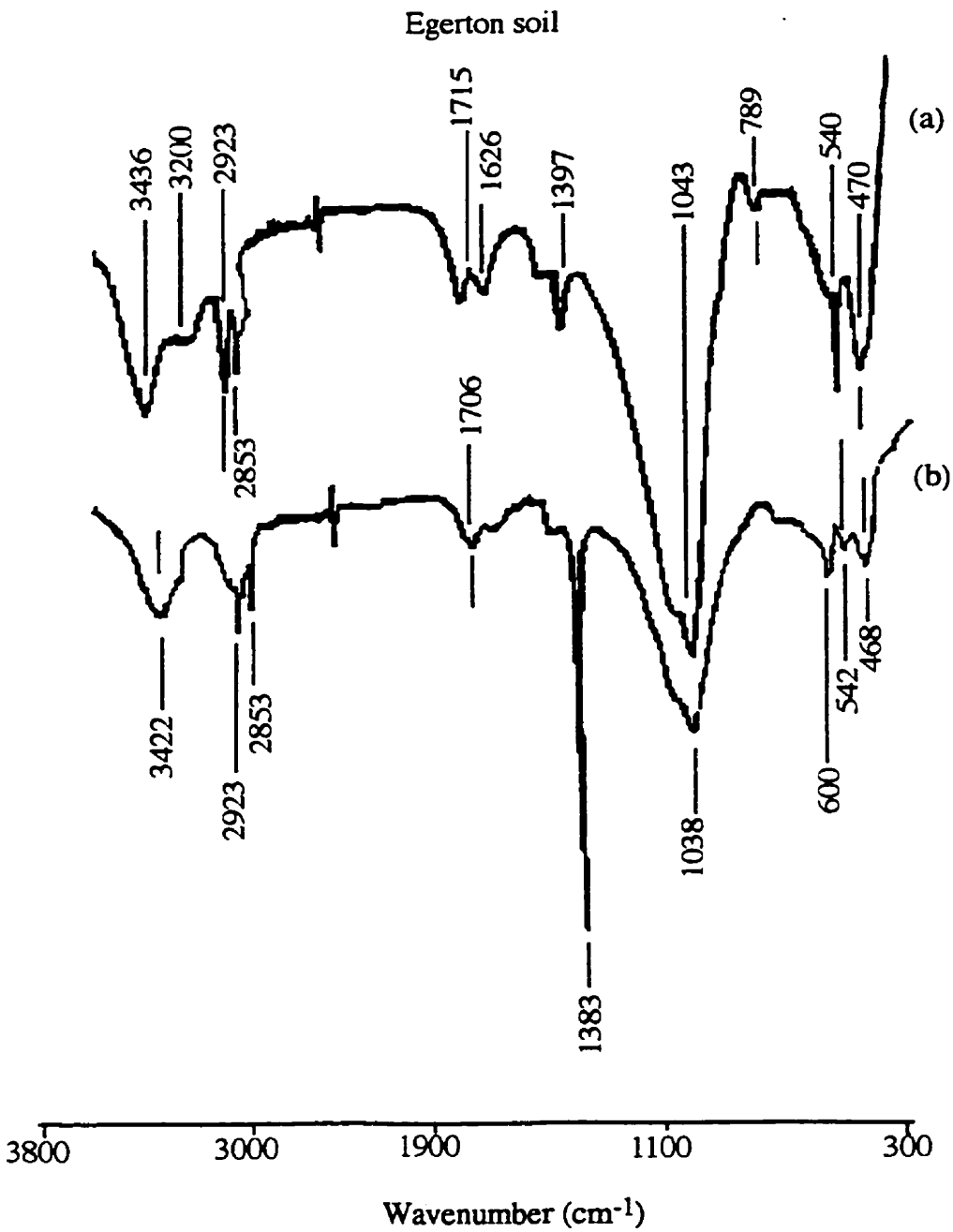

Figure 3.5.9 Effect of heat treatment on infrared spectra of the Egerton soil treated with 1 M $NH_4H_2PO_4$ for 100 days at 25 °C. (a) control soil and (b) heat treatment at 110 °C in air for 2 h

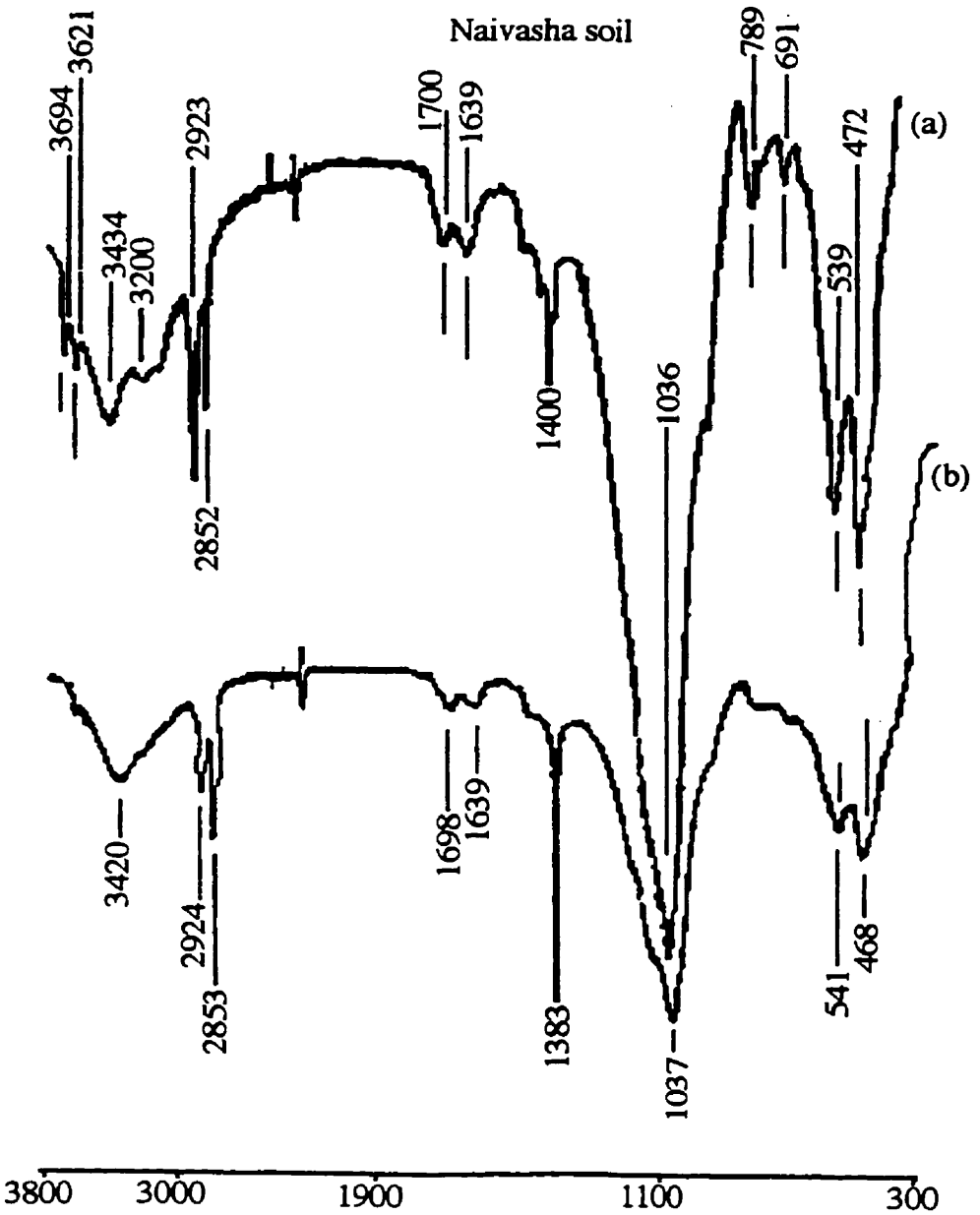

Figure 3.5.10 Effect of heat treatment on infrared spectra of the Naivasha soil treated with 1 M $NH_4H_2PO_4$ for 100 days at 25 °C. (a) control soil and (b) heat treatment at 110 °C in air for 2 h

The absolute amount of Cd released cannot be interpreted in terms of pH in the system studied since the pH of the soil-$NH_4H_2PO_4$ suspension at the end of the 15-min reaction period was in the order: Naivasha (5.09) > Egerton (4.97) > Soy (4.66). When Cd was added to the surface soils, the Naivasha soil released the lowest amount of Cd, indicating that compared with the other soils, the Cd added was more strongly retained by the Naivasha soil and thus, limited in its release. This could be attributed to the Mn content of the surface horizon of the Naivasha soil which was one order of magnitude higher compared to the Egerton or Soy soil. Increasing the concentrations of $NH_4H_2PO_4$ increased the amounts of Cd released during the reaction period of 0.25 to 1 h. This would imply that at the fertilizer granule-soil interface where the concentration of orthophosphate is expected to be high, more Cd would be solubilized compared to the bulk soil.

The zero-order or the first-order rate equation described the kinetics of Cd release during the 0.25 to 1h by 1.00 M $NH_4H_2PO_4$ solution virtually equally well. The rate constants calculated from the zero-order equation for the Cd released from the soils treated with the Idaho MAP fertilizer or the Cd perchlorate-added MAP chemical reagent varied with the soil type and form of Cd added to soil. The rate constants for the Cd release by 1 M $NH_4H_2PO_4$ solution from the soils treated with the Idaho MAP fertilizer were one order of magnitude higher, compared to the rate constants for the Cd released by the deionized distilled water from the soils with the same treatments. This indicated that the rate of Cd release from the soils was greatly enhanced by application of the Idaho MAP fertilizer. The combined effect of Cd present in the Idaho MAP-fertilizer and the phosphate would enhance the rate of Cd release from the soils.

The NH_4-taranakite was identified in the Egerton and the Naivasha soils treated with 1 M $NH_4H_2PO_4$ solution using X-ray diffraction analysis. However, NH_4-taranakite did not form when monoammonium phosphate was spiked with Cd even at 6.4 x 10^{-3} M $Cd(ClO_4)_2$, indicating that Cd perturbs the formation of taranakites in soils. The

nature of the soil-fertilizer reaction products depends to a large extent upon the acidity developed during dissolution of the applied fertilizer and may also vary with the distance from the fertilizer granule because of the change of phosphate concentration. In the immediate vicinity of the fertilizer granule the phosphate concentration is saturated. High concentrations of phosphate can cause substantial alterations of soil constituents and subsequent release of metal ions. Since plants obtain most of their fertilizer phosphorus from reaction products and not from the fertilizer per se, the identification of reaction products is of primary importance in understanding the nature and behavior of phosphorus in soils. The formation of NH_4-taranakite may lead to the conversion of some of the N and P in the fertilizer to slowly available forms in the soils.

Phosphate fertilizers contain Cd as a contaminant and their application to soils is known to lead to Cd accumulation in soils. In this study, it has also been demonstrated that the application of phosphate fertilizers to soils may promote Cd release from soils, thus increasing the Cd content in soil solution. This may lead to increased Cd uptake by plants and adverse effects on human health. The results presented in this investigation highlight the influence of the Idaho MAP fertilizer applied to agricultural soils on Cd release. This study also shows that NH_4-taranakite can form in the acidic tropical soils when monoammonium phosphates are applied to these soils. However, in the fertilizer granule-soil interface, the formation of NH_4-taranakite may be perturbed by Cd, if the applied MAP fertilizer contains sufficiently high Cd as an impurity.

4. GENERAL DISCUSSION AND CONCLUSIONS

The background Cd content of soils can provide useful information on the geographical variations of this element in soil environments. The total Cd content of soils is related to the Cd content of the original rock on which the soil is developed, as well as the alterations undergone by these starting materials. Determination of Cd distribution among various chemical forms in soils is of importance in understanding the chemistry of soil Cd in relation to its mobility and bioavailability. Most studies involving Cd have been limited to temperate soils. To date, information on the Cd status and speciation in tropical soils is lacking in literature.

The present study (Section 3.1) showed that both the Cd content and the Cd availability index (AAAc-EDTA extractable Cd) of the selected soil profiles from the main agricultural areas in Kenya varied with the soil type and generally decreased with depth. It has been reported that Cd is either present quite evenly throughout a given soil profile (Adriano, 1986) or accumulates at the surface horizon in parallel with the humus (Andersson, 1977; Adriano, 1986). The Cd concentrations in the soil profiles were significantly correlated with the pH of the soils ($r = 0.752$, $p = 1.2 \times 10^{-3}$) (Table 3.1.6). The study also indicated that the Cd content of the soils varied with the parent materials. The Cd content of the Egerton soil (derived from volcanic ash), the Naivasha soil (derived from lacustrine deposits, mainly of volcanic ash origin) and the Kericho (derived from volcanic ash) were higher compared to the Kitale soil (derived from metamorphic rocks) or the Soy soil (derived from igneous rocks). The Cd contents of the surface soils were in the following order: Egerton (0.157 mg kg^{-1}) > Naivasha (0.119 mg kg^{-1}) > Kericho

(0.047 mg kg^{-1}) > Soy (0.019 mg kg^{-1}) > Kitale (0.017 mg kg^{-1}). This sequence of Cd concentration of the soils studied appears to be in agreement with the geochemistry of Cd. Page and Bingham (1973) suggest that the soils derived from igneous rocks would have Cd contents of 0.1-0.3 mg kg^{-1}, those on metamorphic rocks would contain 0.1-1.0 mg kg^{-1} and those derived from sedimentary rocks 0.3-11 mg kg^{-1} Cd. In general, most soils can be expected to contain < 1 mg kg^{-1}, except those contaminated from discrete sources or developed on parent materials with anomalously high Cd contents, such as black shales (Alloway, 1995). The range of Cd concentrations in the parent materials would depend upon the composition of the rock. The Cd content in the various rock components have been reported as follows: igneous rocks: rhyolites (0.03-0.57 mg kg^{-1}), granites (0.01-1.60 mg kg^{-1}), basalts (0.01-1.60 mg kg^{-1}); metamorphic rocks: gneisses (0.007-0.26 mg kg^{-1}), schists (0.005-0.87 mg kg^{-1}) and sedimentary rocks: shales and clays (0.017-11 mg kg^{-1}), black shales (0.30-219.0 mg kg^{-1}) and sandstones and conglomerates (0.019-0.4 mg kg^{-1}) (Alloway, 1995). The Cd content of soils derived from volcanic ash can be as high as 4.5 mg kg^{-1} soil (Bailey et al., 1995). Cadmium content of soils is determined not only by the parent material but also by its subsequent alterations through weathering processes (Tiller, 1989). Besides the parent materials, the differences in the Cd content of the soils used in the present study (Table 3.1.2) could be partially attributed to the different weathering intensity in these areas which leads to variations in soil pH. Both Soy and Kitale soils are Oxisols; the high weathering intensity apparently contribute to the depletion of the Cd level in these two soils.

The Cd content of the surface horizons used in this study were on average 27% of that of the temperate soils from the Canadian Prairies (Krishnamurti et al., 1997a). The sequential chemical extraction method showed that Cd was neither present in exchangeable nor in carbonate-bound form and that metal-organic complex bound-Cd species was, on average, the most predominant in the surface soils. In the subsurface soils, Cd was present mainly in the residual form. The metal-organic complex bound-Cd

significantly correlated with the Cd availability index of these tropical soil profiles, indicating the importance of metal-organic complex-bound Cd in contributing to the Cd availability in the soils. Further, it was shown that the organic-bound Cd significantly correlated with Cd availability index; however, there was no collinearity between the organic-bound Cd and the metal-organic complex-bound Cd, indicating that the two forms of particulate-bound Cd are not from the same binding site. Krishnamurti et al. (1995a) showed that metal-organic complex-bound Cd is the most predominant particulate-bound Cd species in the surface soils in the Canadian Prairies. The metal-organic complex-bound Cd is most significantly correlated with the Cd availability index of the temperate soils (Krishnamurti et al., 1997b). A comparison of the percent distribution of particulate-bound Cd species in the Canadian Prairies and the tropical soils in Kenya is presented in Appendix 6.7. The metal-organic complex-bound Cd, on average, accounted for 40.5% and 37.1% of the total soil Cd in the temperate and tropical soils, respectively. The present study, therefore, highlights a frequency distribution of the metal-organic complex-bound Cd in both tropical and temperate soils. The information obtained from the study of Cd content and speciation in the soils is fundamental for establishing a Cd database and in interpreting the importance of Cd speciation in Cd bioavailability in tropical soils.

Besides the natural soil Cd, the application of phosphate fertilizers to acidic tropical soils by farmers in Kenya to correct phosphorus deficiency may lead to Cd accumulation in these soils. The fate of Cd introduced to soils will be controlled by a series of chemical reactions and a number of physical and biological processes in soil environments. The slow soil processes over several years may change the forms, extractability and bioavailability of the metals (Bell et al., 1991). Street et al. (1978) reported that chemical form of Cd added to soils may affect its solubility, mobility and bioavailability in the soil. Monoammonium phosphate fertilizers contain a wide range of Cd (8 to 174 mg Cd kg^{-1}) as a contaminant (Williams and David, 1976; He and Singh, 1994b; Kpomblekou and Tabatabai, 1994). The impact of interaction of phosphate

fertilizers added to tropical soils on long-term Cd accumulation and transformation in the soils remains to be uncovered. Phosphate fertilizers used in Kenya are from a variety of sources. Monoammonium phosphate (MAP) is one of the fertilizers used in Kenya and could contribute to contamination of Cd to the soils sampled for this study (Table 3.1.1). Phosphate fertilizers are commonly used in the Egerton soil which is derived from volcanic ash. In Naivasha, the soils are derived from lacustrine deposits which are of volcanic ash origin. This is a vegetable growing area and most of the farmers use phosphate fertilizers to improve the crop yield. The high phosphate fertilizer application to the Naivasha soil is likely to cause Cd accumulation in this soil. Perennial crops, e.g., tea are grown in the Kericho soil. Phosphate fertilizers are applied especially in the early stages of planting. Further, due to phytocycling of plant residues after cuttings to improve the tea yield, Cd may accumulate in the surface soil. In the Soy and Kitale soils, where maize and wheat crops are grown, the use of phosphate fertilizers especially in commercialized farms can contribute to Cd contamination in these soils.

The effect of residence time on the transformation of Cd introduced to the soils to various particulate-bound Cd species and its impact on Cd availability index was investigated in this study (Section 3.2). Cadmium was introduced to the soils in the form of Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent as described in the incubation procedure (Section 3.2.2.1). The Cd introduced to the soils was transformed to a series of particulate-bound Cd species. Changes in individual particulate-bound Cd species with time in the treated soils showed that except for the residual Cd species which steadily increased with the incubation time, the rest of the particulate-bound Cd species decreased with time. In the natural soils (Section 3.1.3.3), statistical analysis showed that the residual Cd was significantly related to Cd availability ($r = 0.795$, $P = 3.94 \times 10^{-4}$); however, the level of significance of the correlation of the organic-bound Cd ($r = 0.914$, $p = 1.87 \times 10^{-6}$) and the metal-organic complex-bound Cd ($r = 0.960$, $P = 1.53 \times 10^{-8}$) with the Cd availability index were two and four orders of magnitude,

respectively, higher compared with the residual Cd (Table 3.1.8). With time the residual Cd increased, suggesting that the added Cd was transformed to less soluble forms. The study also showed that metal-organic complex bound Cd was the most predominant Cd species formed and this particulate-bound Cd species steadily decreased with increasing residence time in the tropical soils studied.

The M NH_4Cl was used to examine the effect of residence time on Cd availability of the treated soils. It was reported in section 3.2.2.3 that stability constants of Cd-chloride complexes are in the similar order of magnitude as those of the Cd-organic acid complexes of many low-molecular-weight organic acids present in the soil rhizosphere (Krishnamurti et al., 1995b). The study on Cd availability showed that the amounts of M NH_4Cl extractable Cd from the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent decreased with time. The decrease in Cd availability index with residence time indicated that Cd added to the soils was transformed to less soluble forms. The amounts of Cd extracted by M NH_4Cl from the soils treated with the Cd perchlorate-added MAP chemical reagent decreased more rapidly compared to the Cd present as an impurity in the phosphate fertilizer, indicating that Cd present in the phosphate fertilizer apparently might have reacted with the soils to form insoluble reaction products. The forms of Cd present in the Idaho MAP-fertilizer could also account for the observed difference in the amounts of Cd extracted by NH_4Cl from the soils treated with the Idaho MAP-fertilizer and those treated with the Cd perchlorate-added MAP chemical reagent. The effect of residence time on Cd transformation in soils is important in understanding the implications of Cd introduced to soil through management practices and the effect of residual Cd on the ecosystem health. The findings of this study indicated the importance of residence time on Cd transformation and its impact on Cd availability in soils. If Cd is transformed to less available forms with time, there will be less danger of its uptake by plants. However, the effects of farming practices such as crop species and

cropping systems and applications of fertilizers on the dynamics of Cd in soils merit attention.

The low-molecular-weight organic acids (LMWOAs) secreted by plant roots can modify the mobility of Cd through the formation of soluble complexes in the soil rhizosphere (Krishnamurti et al., 1997a). The kind and amount of LMWOAs in the soil rhizosphere vary with crop species and cultivars (Marschner, 1997; Szmigielska et al., 1995, 1997). The influence of LMWOAs on the dynamics of Cd in tropical soils is lacking in the literature, however. The present study (Section 3.3) investigated the kinetics of Cd release by LMWOAs (i.e., acetic, citric, fumaric, malic, oxalic, succinic) from the natural soils. The kinetics of Cd release by acetic, citric and oxalic acids from the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent was also investigated. The data on Cd release by 10^{-2} M LMWOAs indicated that the Cd released from the soils increased initially and then slowly decreased with time and approached a plateau. Cadmium was released into soil solution by the LMWOAs as Cd-LMWOA complexes while the decrease in Cd released with time appeared to be due to readsorption of the released Cd onto soil particle surfaces. The decrease in the amounts of Cd released from the natural soils varied substantially with the nature of LMWOAs. For example, the decrease in the amounts of Cd released was more pronounced with the malic acid than with the acetic acid (Figure 3.3.1). The difference could be attributed to the properties of these acids. Malic acid is a dicarboxylic acid while acetic acid is a monocarboxylic acid. Compared with acetic acid, malic acid may have residual carboxyl group after reaction with the soils to bind the Cd released to solution.

To establish the kinetics of Cd release from the soils by LMWOAs, kinetic models were applied in this study. By using the best fit model, the errors in the calculation of rate constants of Cd release from the soils are minimized. Although the models do not explain the reaction mechanism in heterogeneous systems, the best fit kinetic model does provide a basis for quantifying the rate of Cd released from soils. Absolute amounts of Cd

released from the soils (mg Cd kg^{-1} soil) by LMWOAs were used in the kinetic study. It is suggested that the use of absolute amounts of Cd released instead of fractions of Cd released is a better indicator of the amount of Cd entering the food chain. Parabolic diffusion equation provided the best fit to the Cd release by the LMWOAs from the natural soils and the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent. The parabolic diffusion equation is often used to indicate that diffusion-controlled phenomena are rate-limiting (Sparks, 1987, 1997). If the release of Cd is diffusion controlled, the rate is inversely proportional to the thickness of the diffusion layer or film (Jost 1952, Crank, 1957), possibly the static LMWOA solution or water film surrounding the solid particles. This relationship is expressed as a variation of parabolic diffusion law (Laidler, 1965; Cooke, 1966; Evans and Jurinak, 1976) and was used in the present study to investigate the rate of Cd release from the soils as expressed below:

$$q = Dt^{1/2} + a$$

where q is the amount of Cd released (Cd_r) (mg kg^{-1} soil) in time t; D is the overall diffusion coefficient and a is a constant. The D values obtained from the parabolic diffusion law are termed as "overall diffusion coefficients" (Evans and Jurinak, 1976) or "apparent diffusion coefficient" (Sparks, 1997). Hodges and Johson (1987) stated D as a transport term proportional to the diffusion coefficient. Plots of q, the amount released against $time^{1/2}$, which are linear for many soil reactions, are often used to calculate a diffusion controlled reaction rate (Cooke, 1966; Chute and Quirk, 1967; Quirk and Chute, 1968; Evans and Jurinak, 1976; Sparks and Jardine, 1981; Jardine and Sparks, 1984; Hodges and Johnson, 1987; Krishanmurti et al., 1992, 1993; Krishanamurti et al., 1997a). Cooke (1966) reported that this equation is valid for the reaction rates in soils measured over relatively short periods, e.g., not much greater than 2 h. For example Cooke (1966) reported that the release of P from the soil-solid phase is a complex reaction to which it is difficult to apply basic kinetic theory with precision. Nevertheless the empirical relationship, $q = Dt^{1/2} + a$, enables a single parameter D to be assigned to the

rate of, e.g., Cd release from the soil. Both transport and chemical reactions can affect the reaction rate in soils. Transport processes include: (1) transport in the soil solution, (2) transport accross a liquid film at the solid-liquid interface, (3) transport in the liquid-filled macropore, (4) diffusion of a sorbate at the surface of the soil, (5) diffusion of a sorbate occluded in a micropore, and (6) diffusion in the bulk of the solid (Sparks, 1997). The actual chemical reaction at the surface is usually instantaneous. In the present study in which the Cd released by LMWOAs was studied in soil suspensions; the data indicate that the Cd release is apparently a diffusion-controlled process. The overall diffusion coefficient was therefore, taken as a measure of the rate of Cd release from the soils by LMWOAs. The rates of Cd release varied with the Cd content and the speciation of the soils. The lowest Cd release rate was observed in the surface of the natural Soy soil (Table 3.3.8). The amounts of metal-organic complex-bound Cd and the organic-bound Cd of the surface horizon of the natural Naivasha and Egerton soils were one order of magnitude higher than those of the Soy soil (Table 3.1.7). This explains the observation that the rate of Cd released from the Naivasha or the Egerton soil was higher than that from the Soy soil. The study indicated that the rate of Cd release by each organic ligand apparently varied with the nature of the particulate-bound Cd species of the soils. In the treated soils, the overall diffusion coefficient values were substantially higher compared to those of natural soils (Tables 3.3.8 and 3.3.9). This indicates that application of the Idaho MAP fertilizer enhanced the rate of Cd released from the soils by LMWOAs.

The excretion of LMWOAs by roots into the soil rhizosphere is a dynamic process. The present study showed that increasing amounts of Cd were released from the natural and treated soils to the soil solution upon renewal of LMWOAs in the soil solution (Figures 3.3.4 and 3.3.5), indicating that the release of LMWOAs would continuously mobilize the release of Cd at the soil-root interface through the formation of soluble Cd-LMWOA complexes. Mench et al. (1988) reported that metal cations were complexed in the soil rhizosphere by a variety of LMWOAs. The formation of Cd-LMWOA complexes

disturbs the equilibrium between the labile metal on the solid phase and soil solution and, thus, enhances the release of the metal to the solution. The removal of Cd^{2+} in soil solution by the plant would establish a diffusion gradient to transport more of the metal to the root surface. The complexation process is reflected in the increase of the amount of the Cd released from the natural soils and the treated soils with the increase in the log stability constants of the Cd-LMWOA complexes as shown in Figure 3.3.3. The rates of Cd release by LMWOAs from the three surface horizons of the natural tropical soils studied (Table 3.3.8) were up to one order of magnitude lower than those of the surface horizons of the three natural temperate soils in the Canadian Prairies (Krishnamurti et al., 1997a). The amounts of the metal-organic complex-bound Cd and the organic-bound Cd of the tropical soils were, respectively, 24% and 20% of those of the temperate soils (Krishnamurti et al., 1995a) (Appendix 6.8). This indicated that the effectiveness of the LMWOAs in influencing the rate of Cd released from the soils varied with their Cd speciation.

The findings of this study showed that LMWOAs commonly present in the soil rhizosphere are effective in enhancing the Cd release from the tropical soils. This would result in the increased Cd release to soil solution especially in the soils treated with phosphate fertilizers which contain high amount of Cd. The results of this study are fundamental in narrowing the gap in knowledge between the temperate soils and the tropical soils in terms of Cd release from the soils by LMWOAs. The role of LMWOAs excreted by plant roots in mobilizing Cd in soils merits attention in order to understand the dynamics of Cd in tropical soils as influenced by cropping systems.

Cadmium complexes readily with chloride and this complexation may influence its mobility and availability (Bingham, et al., 1983; 1984; McLaughlin et al., 1996). When the KCl fertilizers are applied to soils, the concentration of dissolved Cl ions in the immediate vicinity of fertilizer granules can be higher than 1 M (Sakurai and Huang, 1996). Potassium chloride has been shown to greatly enhance the release of Mn from

soils (Krishnamurti and Huang, 1992, 1993; Tu, et al., 1995). Potash (KCl) fertilizers are applied to the K-deficient tropical soils to avoid the depletion of this nutrient by plants. Information on the influence of KCl fertilizer on Cd release from tropical soils is lacking in the literature. Further, monoammonium phosphate (MAP) fertilizers have a wide range of Cd content (8 to 174 mg Cd kg^{-1}) (Williams and David, 1976; He and Singh, 1994b; Kpomblekou and Tabatabai, 1994;). The impact of interactions of MAP and KCl fertilizers on the dynamics of soil Cd remains to be uncovered. The present study (Section 3.4) showed that the amounts of Cd released by KCl chemical or KCl fertilizer from the natural and the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent increased during the 0.25 to 1 h-reaction period and then decreased slightly and tended to reach a plateau (Figure 3.4.1). The influence of KCl on Cd release was largely attributed to the effects of Cd-chloride complexation and the ionic strength of the solution. The effect of K^+ ion competing for the adsorption sites with Cd^{2+} was not evident in natural soils due to the lack of exchangeable Cd of the soils. Even in the MAP-fertilizer treated soils, the effect of K ion on Cd release from the soils was apparently negligible since very small amounts (0.4%) were present in the treated soils. The initial decrease in the amount of Cd released was attributed to the readsorption of the released Cd on the surface of soil particles.

The parabolic diffusion equation was chosen as the best mathematical model to investigate the rates of Cd release from the soils by KCl chemical reagent and fertilizer. The overall diffusion coefficient (D) calculated from the parabolic diffusion equation was taken as a measure of the rate of Cd released by KCl from the soils. The use of parabolic diffusion equation to study kinetics of reactions in soils was explained above under the kinetics of Cd release from the soils by LMWOAs. If the Cd release from the soils is diffusion controlled, the rate is inversely proportional to the thickness of the diffusion layer or film (Jost, 1952; Crank, 1957), possibly the static KCl solution or water film surrounding the solid particles. The rates of Cd released from the natural Naivasha and

Egerton soils (Table 3.4.5) were much higher than from the natural Soy soil. In the Naivasha and Egerton soils, the amounts of metal-organic complex-bound Cd and organic-bound Cd were one order of magnitude, respectively, higher than those of the Soy soil (Table 3.17). This explains the difference in the rates of Cd released from the natural soils. The rates of Cd released from the soils treated with the Idaho MAP-fertilizer or Cd perchlorate-added chemical reagent varied with the soil and the form of Cd introduced to the soil (Table 3.4.6). In the case of the treated soils, the rates of Cd released by KCl chemical or KCl fertilizer were at least one order of magnitude higher compared to those for the Cd release by deionized distilled water, indicating that KCl substantially enhanced the release of Cd from the soils.

It was observed that the rates of Cd released from the natural soils by KCl chemical or KCl fertilizer (Table 3.4.5) and the LMWOAs (Table 3.3.8) were of the same order of magnitude, however, the concentration of KCl (1 M) was about two orders of magnitude higher than that of the LMWOAs (10^{-2} M) used in this study. The data indicated the effectiveness of the LMWOAs, which are commonly found in the soil rhizosphere, in releasing the soil Cd to the solution. In the humid tropical soils where decomposition rate of plant material and the turnover rate of organic matter are high, the application of KCl fertilizers coupled with the rapid formation of LMWOAs from the transformation of plant material would substantially enhance the release of Cd. The rates of Cd released from the soils treated with the Idaho MAP fertilizer were lower than those of the soils treated with the Cd perchlorate-added chemical reagent (Table 3.4.6). This trend was not evident in the Cd released from the soils by the LMWOAs (Table 3.3.9). This may be attributed to the effectiveness of LMWOAs in releasing Cd from the soils as discussed above.

The present study indicated that application of KCl fertilizers to tropical soils would promote the release of Cd to the soil solution through complexation of chloride at the KCl fertilizer granule-soil interface. Further, the chloride introduced to soils from

potash fertilizer would stabilize Cd-chloride complexes and facilitate their movement in soils. This is of significance especially in the tropics where KCl fertilizers are used to supplement the K supplying power of these soils. Besides KCl fertilizers, phosphate fertilizers are needed to sustain crop production. The data obtained in the present study indicate that the application of phosphate fertilizers of high Cd content along with KCl fertilizer would substantially enhance the rate of Cd released from the soils, which may lead to contamination of the terrestrial food chain. Among the soils studied, this information is especially of significance to the Naivasha soil where farmers heavily apply KCl and phosphate fertilizers to the vegetable farms. Therefore, the application of KCl fertilizers together with phosphate fertilizers, which contain high Cd content, should be conducted with care.

The presence of high concentrations of phosphate in the vicinity of phosphate fertilizer zone of soil can cause dissolution of soil minerals (Sample et al., 1980; Lindsay et al., 1989; Tisdale et al., 1993). In the tropical soils, phosphorus deficiency is experienced due to its fixation by these soils. Phosphate fertilizers are, therefore, applied to correct the phosphorus deficiency. Monoammonium phosphate has been shown to induce K release from soils (Zhou and Huang, 1995). However, the information on phosphate-induced Cd release from tropical soils is lacking in the literature. The present study (Section 3.5) showed that 1 M $NH_4H_2PO_4$ solution induced the release of Cd from the natural soils and the soils treated with the Idaho MAP-fertilizer or the Cd perchlorate-added MAP chemical reagent. The enhanced release of Cd by the phosphate was attributed to the combined effect of Cd introduced to the soils and the Cd released from the soils through the attack of the protons and the complexation of phosphate. The phosphate-induced Cd release from the natural and the treated soils increased during the short-reaction period of 0.25 to 1 h and then decreased with time and tended to approach a plateau (Figure 3.5.4). The decrease of the Cd concentration was apparently due to readsorption of the released Cd onto the surface of soil particles and /or formation of

sparingly soluble reaction products in the solution. The present study showed that the amounts of Cd released by $NH_4H_2PO_4$ increased with the increase in the concentration of $NH_4H_2PO_4$ during the 0.25 to 1 h reaction period. The high phosphate concentration as used in the present study would be expected at the fertilizer granule soil-interface. Lindsay et al. (1962) reported that in the immediate vicinity of phosphate fertilizer granule the pH is quite low (pH = 3.5) and the solution P concentration can be as high as 2.5 M. Phosphate fertilizers are often mixed with seeds or side banded. This therefore, indicates that, at the fertilizer granule-soil interface where the concentration of orthophosphate is high, more Cd would be mobilized compared to the bulk soil. The mobilized Cd in the soil rhizosphere can be transported to the plant root and would then be taken up by the plant. This could lead to the contamination of the food chain. The content of total Cd, the metal-organic complex-bound Cd, and the organic-bound Cd of the surface horizon of the Soy soil were two orders of magnitude lower than those of the other soils studied (Table 3.1.7). This accounts for the lower amounts of Cd released from the Soy soil compared with the other two soils (Table 3.5.1).

When Cd was added to the surface soils, the Naivasha soil released the lowest amount of Cd (Table 3.5.2), indicating that compared with other soils, the Cd added was retained more strongly by the Naivasha soil, thus limiting it release. According to Jenne (1968), the retention capacity for divalent metals is determined primarily by the quantities of organic C, and oxides of Fe and Mn present in soils because these components have high affinities for metallic cations. Since the amounts of the extractable Fe and the organic C of the Naivasha soil were lower than those of the Egerton and Soy soils, the retention of Cd by the surface horizon of the Naivasha soil could be attributed to the presence of Mn in the surface horizon which was one order of magnitude higher compared to the Egerton or the Soy soil (Table 3.1.2). The oxides of Mn are good adsorbents for heavy metals in the soil environments (McKenzie, 1980). In the Soy soil which had low contents of sorptive soil components (Fe, Mn, etc.), least retention of Cd may be

expected. This may have adverse health implications as the Cd released to the soil solution may be taken up by the plants.

The zero-order rate equation was chosen as the best fit kinetic model to calculate the rates of Cd release from the soils by MAP. The zero-order model was also reported to best fit the kinetic data of the phosphate-induced K released from temperate and tropical soils (Zhou and Huang, 1995).The rates of Cd release for the treated soils varied with the soil type and the form of Cd added to soils. The rate constants for Cd release by M $NH_4H_2PO_4$ solution from the soils treated with the Idaho MAP-fertilizer were one order of magnitude higher, compared to the rate constants for the Cd released by deionized distilled water from the soils with the same treatments. The study showed that the application of the Idaho MAP-fertilizer greatly enhanced the rate of Cd released from the soils. The present study indicated that the combined effect of Cd present in the Idaho MAP-fertilizer and the phosphate would enhance the rate of Cd release from the soils. It was also observed that the rates of Cd release by M $NH_4H_2PO_4$ (Table 3.5.4), 10^{-2} M LMWOAs (Table 3.3.8) and M KCl (Table 3.4.5) from the natural soils were in the same order of magnitude. This is due to the effectiveness of LMWOAs in enhancing Cd release from the soils. The study indicated that the application of phosphate fertilizers, which contain high Cd content, to tropical soils would enhance the Cd release from the soils. Considering that large amounts of phosphate fertilizers are required to sustain crop production in the tropical soils and a wide variety of phosphate fertilizers are becoming available to farmers in developing countries, the impact of phosphate fertilizer application to tropical soils on Cd release, thus, should not be overlooked for years to come.

Ammonium taranakite was identified as a reaction product of the 1 M $NH_4H_2PO_4$ with the soils studied (Figures 3.5.5 and 3.5.6) using X-ray diffraction analysis. The amount of taranakite formed would depend, in part, on the amount of the Al released from the soils. Usually, taranakites form more readily in highly weathered soils which are rich in Al oxides (Prabhudesai and Kadrekar, 1984). The formation of ammonium taranakite

in the immediate vicinity of phosphate fertilizer zone can lead to the transformation of N and P from readily available to slowly available form. However, the present study revealed that ammonium taranakite did not form when monoammonium phosphate was spiked with Cd at 6.4 x 10^{-3} M $Cd(ClO_4)_2$, indicating that Cd can perturb the formation of taranakites in soils (Figure 3.5.5). The Cd concentration studied was in the range of Cd concentrations in soil solution in the fertilizer granule-soil interface (Appendix 6.1). The perturbation of the taranakite formation can be attributed to complexation of the Cd with the phosphate (log stability constant of Cd-phosphate complex = 2.91) (Smith and Martell, 1976) which affected the nucleation of the taranakite and the growth of the taranakite crystals. Therefore, the formation of ammonium taranakite in the immediate vicinity of the fertilizer zone may be perturbed if the phosphate fertilizer applied contains sufficiently high concentrations of Cd. This would, in turn, influence the transformation of N and P. The long-term application of phosphate fertilizers to agricultural soils may greatly influence the transformation and dynamics of Cd in the soils. The impact of phosphate fertilization on the environmental quality, food chain contamination, and ecosystem health, should thus, be of concern.

In summary, the present study revealed the speciation and dynamics of Cd of Kenyan soils. This is fundamental for establishing the Cd database in tropical soils and is of significance in interpreting the importance of Cd speciation in soil Cd availability . The study showed that , although the residual Cd was relatively abundant in some surface soils studied, metal-organic complex-bound Cd was, on average, the most predominant particulate-bound Cd species in the surface horizon of the natural tropical soils in Kenya. The study showed the significance of residence time on Cd transformation in soils and its impact on Cd availability index of the soils. The Cd introduced to soils was shown to transform to less available forms with time. However, the impact of farming practices on residual effect of Cd accumulated in soils should receive increasing attention. The effectiveness of LMWOAs, which should vary with crops and cropping systems, in

releasing Cd from the tropical soils to soil solution was demonstrated in the present study. In the temperate soils which had higher content of total and labile particulate-bound species Cd (Krishnamurti et al., 1997a) than the tropical soils, the LMWOAs released substantially higher amounts of Cd than in the case of the tropical soils studied. However, when Cd was introduced as an impurity in the Idaho MAP-fertilizer to the tropical soils, substantially higher release rates of Cd by LMWOAs were observed compared to control soils. The application of KCl and phosphate fertilizers together to agricultural soils may greatly enhance the release of Cd to soil solution. The formation of phosphate reaction product such as taranakite in the acidic tropical soils can also lead to the transformation of N and P to slowly available forms. However, the present study indicated that the application of phosphate fertilizers high in Cd content may perturb the formation of taranakites in soil. In view of the results presented in the present study, the impact of farming practices such as fertilizer use, crops and cropping systems on the speciation, dynamics and phytoavailability of soil Cd and its contamination to the food chain deserves close attention.

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6. APPENDIX

6.1 Sample calculation for the amount of cadmium added to the soil in the incubation study

Recommended rate of monoammonium phosphate fertilizer application: 130 kg/ha

Cd content of Idaho MAP-fertilizer : 144 mg/kg

Amount of Cd introduced to soil from the fertilizer: 130 kg/ha MAP x 144 mg/kg

= 18720 mg Cd/ha

= 18.72 g Cd/ha

Amount of fertilizer in 1 m^2 plot = 130 kg/10^4 = 0.013 kg

= 13 g of fertilizer

Amount of soil in contact with fertilizer:

For a spherical fertilizer granule with a diameter of 3 mm (0.3 cm)

Volume of a fertilizer granule = 4/3 πr^3

(r is the radius of fertilizer granule = 0.15 cm) = 4/3 x 3.14 x $(0.15)^3$ cm^3

= 0.0141 cm^3

Thickness of soil around fertilizer granule = 1 mm = 0.1 cm

Radius of a fertilizer granule and soil around it = 0.15 + 0.1 = 0.25 cm

Total volume (fertilizer granule + soil around it) = 4/3 x 3.14 $(0.25)^3$ = 0.0654 cm^3

Vol. of the soil around the fertilizer granule = 0.0654 - 0.0141 cm^3

= 0.0513 cm^3

Bulk density of the soil = 1.49 g cm^{-3}

Weight of the soil around 1fertilizer granule = 0.0513 x 1.49 g

= 0.0764 g soil

Weight of MAP fertilizer in 1 m^2 plot = 13 g (equivalent to 392 MAP fertilizer granules)

Therefore, Wt. of soil in 1 m^2 plot around the granules = 0.0764 g x 392 = 30.0 g

Amount of soil around the fertilizer granules in 1 ha $= \frac{30.0 \times 10^4}{1000}$

= 300.0 kg soil

Hence 18.72 g Cd (from the Idaho MAP-fertilizer) is present in 300.0 kg soil

Amount of Cd in 1 kg soil $= \frac{18.72}{300.0}$

= 0.0624 g Cd/kg soil

Hence amount of Cd used in the incubation study = 62.4 mg Cd kg^{-1} soil

= 6.24 mg of Cd/100 g soil

= 0.0062 g Cd/100 g soil

Amount of $Cd(ClO_4)_2 . 6H_2O$ required for 100 g soil

$Cd(ClO_4)_2 .6H_2O$ FW = 419.3

Weight of Cd perchlorate taken = $\frac{419}{112.4}$ x 0.0062 g = 0.0231 g Cadmium perchlorate

Sample calculation for the Cd concentration in the fertilizer granule-soil interface

Field capacity of the soils were: Egerton, 30%, Naivasha, 29% and Soy 20%.

Weight of Cd perchlorate added to 100g soil = 0.0231g

Solution Cd concentration at the 20% field capacity $= \frac{0.0231 \times 1000}{419 \times 20}$

$= 2.8 \times 10^{-3}$ M

Appendix 6.2 Analytical data on the saturated soil extract †

Soil	Depth cm	pH (paste)	EC $mScm^{-1}$	Soluble ions						
				Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Cl^{-}	NO_3^{-}	SO_4^{2-}
				mol L^{-1}						
Egerton	0-40	5.6	0.33	7×10^{-4}	4×10^{-4}	1×10^{-3}	4×10^{-4}	5×10^{-4}	3×10^{-4}	2×10^{-4}
	40-70	5.6	0.18	2×10^{-4}	1×10^{-4}	3×10^{-4}	1×10^{-3}	5×10^{-4}	2×10^{-5}	2×10^{-4}
	70-100	5.8	0.17	4×10^{-4}	3×10^{-4}	2×10^{-4}	2×10^{-3}	4×10^{-4}	2×10^{-5}	2×10^{-4}
Naivasha	0-40	6.1	1.36	9×10^{-4}	1×10^{-3}	1×10^{-3}	0.016	3×10^{-3}	7×10^{-7}	4×10^{-3}
	40-70	7.4	4.78	3×10^{-3}	1×10^{-3}	2×10^{-3}	0.047	5×10^{-3}	7×10^{-4}	0.03
	70-100	7.8	5.26	5×10^{-3}	2×10^{-3}	3×10^{-3}	0.046	4×10^{-3}	7×10^{-4}	0.02
Kericho	0-40	4.1	0.22	3×10^{-4}	10×10^{-5}	3×10^{-4}	2×10^{-4}	3×10^{-4}	1×10^{-3}	2×10^{-4}
	40-70	4.4	0.12	1×10^{-4}	7×10^{-5}	2×10^{-4}	2×10^{-4}	2×10^{-4}	7×10^{-4}	5×10^{-5}
	70-100	4.0	0.12	1×10^{-4}	8×10^{-4}	3×10^{-4}	6×10^{-4}	2×10^{-4}	7×10^{-4}	1×10^{-5}
Soy	0-40	5.2	0.25	1×10^{-3}	1×10^{-3}	9×10^{-4}	1×10^{-3}	3×10^{-4}	4×10^{-5}	7×10^{-4}
	40-70	5.3	0.15	8×10^{-4}	5×10^{-4}	3×10^{-4}	5×10^{-4}	4×10^{-4}	1×10^{-5}	2×10^{-4}
	70-100	6.2	0.29	9×10^{-4}	5×10^{-4}	5×10^{-4}	7×10^{-4}	5×10^{-4}	6×10^{-5}	3×10^{-4}
Kitale	0-40	4.9	0.38	7×10^{-4}	9×10^{-4}	1×10^{-3}	1×10^{-3}	8×10^{-4}	5×10^{-6}	4×10^{-4}
	40-70	5.1	0.12	2×10^{-4}	1×10^{-4}	2×10^{-4}	6×10^{-4}	9×10^{-4}	6×10^{-6}	8×10^{-5}
	70-100	5.0	0.08	1×10^{-4}	9×10^{-5}	1×10^{-4}	6×10^{-4}	9×10^{-5}	7×10^{-6}	1×10^{-4}

† The dissolved cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) were determined by atomic absorption spetrophotometer from the soil extracts (Rhoades, 1982). Dissolved anions in soil extracts, e.g., Cl^{-}, NO_3^{-} were determined by autoanalyzer and SO_4^{2-} was calculated from the total S determined by ICP spectrometry.

Appendix 6.3 Some of the minerals identified in the particle size fractions of the soils studied†

Particle size (μm)	Soils‡				
	Egerton	Naivasha	Kericho	Soy	Kitale
0.2	Micas Kaolinite	Micas Kaolinite	Micas Kaolinite	Micas Kaolinite	Micas Kaolinite
0.2-2	Micas Kaolinite	Micas Kaolinite	Micas Kaolinite	Micas Kaolinite	Micas Kaolinte
2-5	Micas Kaolinite Quartz Feldspars	Micas Kaolinite Quartz Feldspars	Micas Kaolinite Quartz Felspars	Micas Kaolinite Quartz Feldspars	Micas Kaolinite Quartz Felspars
5-20	Micas Quartz Feldspars	Micas Quartz Feldspars	Micas Quartz Felspars	Micas Quartz Feldspars	Micas Quartz Feldspars
20-50	Quartz Feldspars	Quartz Feldspars	Quartz Felspars	Quartz Feldspars	Quartz Feldspar
> 50	Quartz Feldspars	Quartz Felspars	Quartz Feldspars	Quartz Feldspars	Quartz Feldspars

† The soil samples were treated sequentially with 1M NaOAc and 30% H_2O_2 prior to XRD analysis. The Fe oxides were not removed. The 0.2, 0.2-2 and 2-5 μm size fractions were examined by Rigaku X-ray diffraction instrument (Tokyo, Japan) using monochromatic Cu-K_α radiation generated at 50 kV-150 mA. The coarse fractions (5-20, 20-50 and > 50 μm) were ground and used for powdered X-ray diffraction analysis by Philips X-ray diffractometer (Model PW 1031) (Eindhoven, the Netherlands) using a Fe-K_α radiation at 35 kV-16 mA.

‡ The oxides of Al (gibbsite), Fe (goethite, hematite) and Mn (Birnessite) were detected in all the particle size fractions of the soils investigated.

Appendix 6.4 Assignment of Infrared bands for the minerals identified in the soil size fractions studied†

Size fraction (μm)	IR bands (cm^{-1})	Assignment	Mineral
< 0.2	3696, 3623, 913	Al--O-H	Kaolinite, mica
	1100, 470, 432	Si-O	Kaolinite, mica
	1032	Si-O-Si	Kaolinite, mica
	1011, 690, 542	Si-O-Al	Kaolinite, mica
0.2-2	3693, 3621, 915	Al--O-H	Kaolinite, mica
	1103, 471, 432	Si-O	Kaolinite, mica
	1033	Si-O-Si	Kaolinite, mica
	1009, 695, 539	Si-O-Al	Kaolinite, mica
2-5	3693, 3621, 913	Al--O-H	Kaolinite, mica
	797, 778	Si-O	Quartz
	1102, 471	Si-O	Kaolinite, mica
	466, 469, 470	Si-O	Feldspars
	1036, 1033	Si-O-Si	Kaolinite, mica
	1009, 696, 539	Si-O-Al	Kaolinite, mica

† The Infrared absorption analysis was conducted using Perkin-Elmer (Model 983) infrared absorption (IR) spectrophotometer (Buckinghamshire, England).

‡ Van der Marel and Beutelspacher (1976).

Appendix 6.5 The FTIR bands of the clay (< 2 μm) fraction of the Egerton soil removed by 0.1 M sodium pyrophosphate treatment†

FTIR band (cm^{-1})	Assignment‡
3434, 3440	OH stretch of phenolic OH, Hydrogen-bonded OH
3300-3465	OH stretch of Al, Fe and Mn
2922, 2924	Aliphatic C-H stretch/asymmetric CH stretch of $-CH_2-$
doublet at 2923-2853	OH stretch of Al, Fe and Mn
2854	Symmetric CH stretch of $-CH_2-$
1708, 1712	C=O stretch of -COOH
1625, 1627	Aromatic C=C stretch and/or asymmetric $-COO^-$ stretch
1656	OH stretch of Al, Fe and Mn
1463	Aliphatic C-H, $-CH_2-$
1384	Symmetric COO^-, aliphatic C-H deformation ($C-CH_3$)
1256	-C-O stretch or OH deformation of COOH, $(CH_3)_3$-C-R vibration

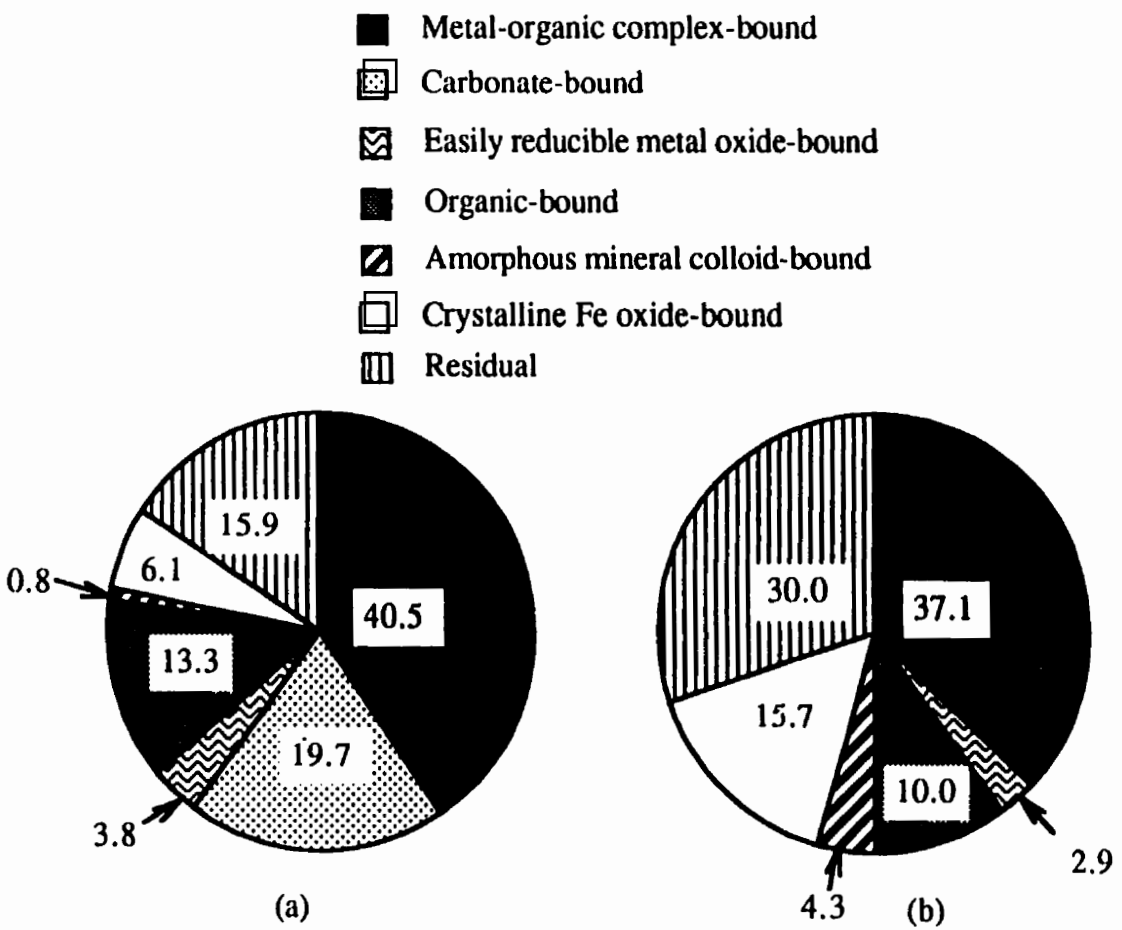
† The FTIR absorption band of the components of the clay size fractions removed by 0.1 M sodium pyrophosphate treatment are shown in the table. The differential FTIR spectrum of the clay fraction before and after the 0.1 M sodium pyrophosphate treatment was obtained using a BioRad/Digilab FTS 40 Fourier transform infrared (FTIR) absorption spectrophotometer (Minnesota, USA). The sesquioxides which are present in the tropical soils can react with the organics to form complexes which act as sites for Cd binding. Ryskin (1974) reported that the FTIR absorption bands at 1656, a doublet at 2925-2853 and at 3300-3465 cm^{-1} are due to -OH stretching frequency of Al, Fe and Mn.

‡ Based on: Baes and Bloom (1989), Bellamy (1975), McLaren and Skujins (1971), and Ryskin (1974).

Appendix 6.6 Surface areas of the soils studied†

Soil	Soil type	Depth (cm)	Surface area ($m^2 g^{-1}$)		Ratio of surface area
			BET-N_2	EGME	$\frac{\text{BET-}N_2}{\text{EGME}}$
Egerton	Andisol	0-40	32.4	66.3	0.49
		40-70	53.7	85.3	0.63
		70-100	59.2	113.9	0.52
Naivasha	Inceptisol	0-40	36.0	79.0	0.46
		40-70	52.6	81.0	0.65
		70-100	58.7	95.2	0.62
Kericho	Alfisol	0-40	64.8	109.2	0.59
		40-70	77.6	122.0	0.64
		70-100	93.0	132.8	0.70
Soy	Oxisol	0-40	36.0	71.1	0.51
		40-70	39.5	75.5	0.52
		70-100	45.7	77.6	0.60
Kitale	Oxisol	0-40	24.6	44.5	0.55
		40-70	30.7	56.1	0.55
		70-100	35.2	58.7	0.60

† The specific surface was determined by ethylene glycol monoethyl ether (EGME) method (Eltantawy and Arnold, 1973) and the BET-N_2 method using Autosorb (Quantochrome Corp., Syosset, N.Y).



Appendix 6.7 Comparison of average percent distribution of particulate-bound Cd species of surface horizons of (a) temperate soils in the Canadian Prairies (Krishnamurti et al., 1995a) and (b) tropical soils in Kenya

Appendix 6.8 Comparison of Cd speciation of surface horizons of temperate and tropical soils

	MOC†	CAR	ERMO	ORG	AMC	CFeO	RES	Sum
	mg kg^{-1} soil							
Temperate soils‡	0.107	0.052	0.010	0.035	0.002	0.016	0.042	0.264
Tropical soils††	0.026	ND	0.002	0.007	0.003	0.011	0.021	0.070

† MOC: metal-organic complex-bound Cd; CAR: carbonate-bound Cd; ERMO: easily reducible metal oxide-bound Cd; ORG: organic-bound Cd; AMC: amorphous mineral colloid-bound Cd; CFeO: crystalline Fe oxide-bound Cd, and RES: residual

‡ Average values of 16 surface soils of major soil types (Chernozemic soils and Luvisol) in the Canadian Prairies (Krishnamurti et al., 1995a)

†† Average values of 5 surface soils of main agricultural soil types (Oxisol, Alfisol, Andisol, and Inceptisol) in Kenya

Appendix 6.9 The statistical analysis of the transformation of particulate-bound Cd species in the treated Egerton soil during the incubation period

Incubation period (days)		Particulate-bound Cd species†							
		Exch.	Carb.	MOC	Org.	ERMO	AMC	CFeO	Resid.
	Cd introduced to soil (mg/kg)	Idaho MAP‡-fertilizer treated							
		mg Cd kg^{-1} soil							
15	62.4	0.57	0.23	30.89	18.04	2.89	1.96	4.21	3.62
50	62.4	0.50	0.21	28.60	16.02	2.58	1.85	4.00	8.65
100	62.4	0.31	0.12	22.57	14.66	1.88	0.99	3.85	18.02
$LSD_{0.05}$		0.02	0.01	0.06	0.05	0.05	0.06	0.06	0.08
$LSD_{0.01}$		0.04	0.02	0.13	0.13	0.09	0.11	0.12	0.14
		MAP chemical + $Cd(ClO_4)_2$ treated							
		mg Cd kg^{-1} soil							
15	62.4	0.68	Nd††	34.84	14.46	3.98	0.96	4.78	2.68
50	62.4	0.40	Nd	33.82	14.27	3.98	0.83	4.65	4.45
100	62.4	0.25	Nd	31.15	12.51	3.56	0.76	4.39	9.77
$LSD_{0.05}$		0.06		0.07	0.09	0.04	0.03	0.05	0.06
$LSD_{0.01}$		0.11		0.14	0.17	0.07	0.05	0.10	0.13

† Exch.: exchangeable; Carb.: carbonate-bound; MOC: metal-organic complex-bound; Org.: organic-bound; ERMO: easily educible metal oxide-bound; AMC: amorphous mineral colloid-bound; CFeO: crystalline Fe oxide-bound, and Resid.: residual

‡ Monoammonium phosphate

†† Not detectable

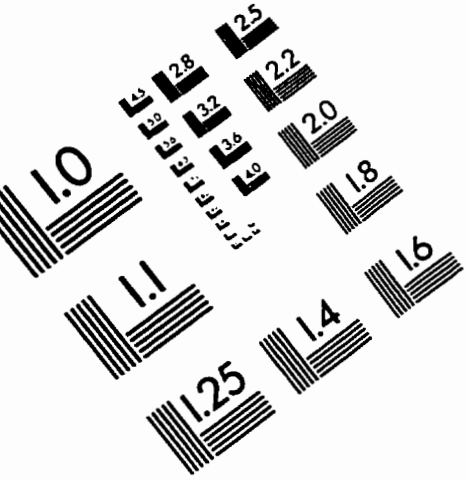
Appendix 6.10 The statistical analysis of the residence time effects on the M ammonium chloride extractable Cd of the treated soils during the incubation period

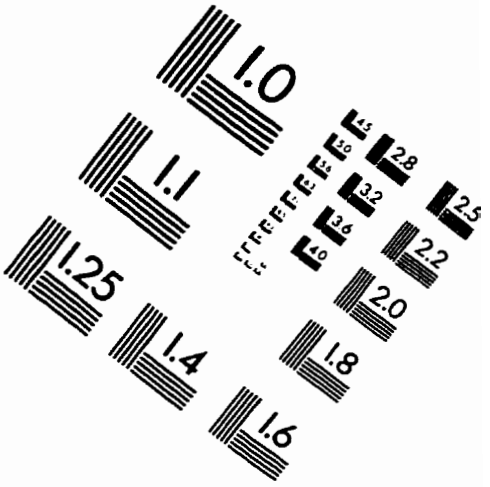
Incubation period (days)	Soils†		
	Egerton	Naivasha	Soy
	Idaho MAP‡-fertilizer treated		
	Extractable Cd (mg kg^{-1} soil)		
15	1.45	1.30	1.37
50	1.28	1.20	1.26
100	1.13	1.04	1.11
$LSD_{0.05}$	0.05	0.06	0.04
$LSD_{0.01}$	0.09	0.13	0.09
	MAP chemical + $Cd(ClO_4)_2$ treated		
	Extractable Cd (mg kg^{-1} soil)		
15	8.93	5.07	8.70
50	6.56	4.70	6.24
100	3.28	2.22	2.41
$LSD_{0.05}$	0.10	0.09	0.06
$LSD_{0.01}$	0.19	0.18	0.10

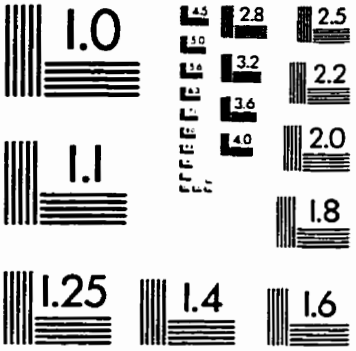
† Amount of Cd introduced to each soil: 64.2 mg kg^{-1} soil

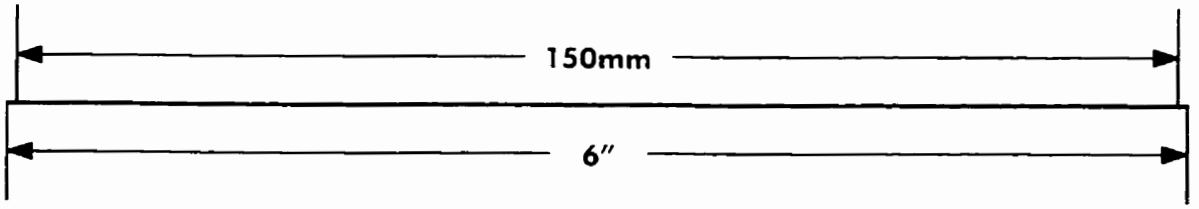
‡ Monoammaonium phosphate

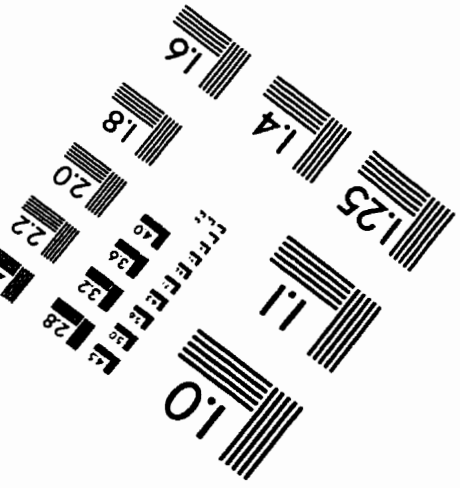
IMAGE EVALUATION
TEST TARGET (QA-3)

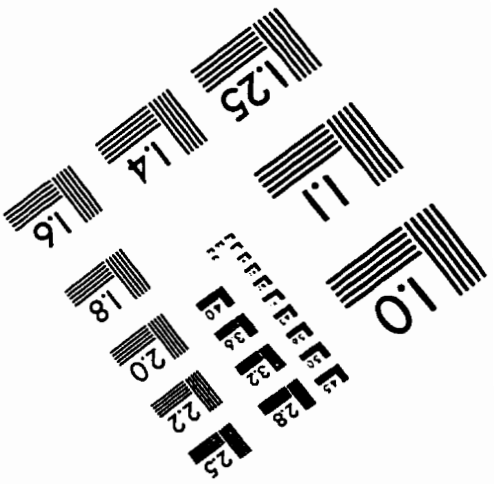












APPLIED IMAGE, Inc
1653 East Main Street
Rochester, NY 14609 USA
Phone: 716/482-0300
Fax: 716/288-5989